LUMINESCENCE
OF LIQUIDS AND SOLIDS

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LUMINESCENCE
OF LIQUIDS AND SOLIDS
and its Practical Applications

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PREFACE

When some twenty-five years ago I began to write my first book on fluorescence and phosphorescence, luminescence was a matter of rather specialized scientific research and I could not hope that the book would arouse much interest outside of physical or chemical laboratories. Since then the practical application of luminescence has gained, slowly at first, an ever increasing importance. For proof one need only consider the part it plays in such diversified fields as vitamin analysis, television, black-out lighting, and petroleum prospecting. The large number of books dealing with the application of luminescence, which have been published in the last decade in the United States, in England, in Germany and in France, is an evident symptom of the growing interest in these problems. Even a monthly journal endeavors to inform us of the latest advances in the use of fluorescent materials.

The existence of so many books is not sufficient reason for increasing their number by still another one, especially since some of them are excellent works and almost every one contains an enormous amount of information. However, this information frequently fails to discriminate between the reliable and useful on one hand and the doubtful or merely accidental on the other. Also, none of these books deals with the entire subject. As a matter of fact, they are all written by specialists interested in one restricted field, be it chemistry, physiology, criminology, mineralogy, or industrial engineering. The physicist's side of the problems is somewhat neglected, as a rule, and after all, luminescence is essentially physics. Moreover, the only two existing detailed monographs on the physics of luminescence are fifteen years old. They have long been out of print and are far from up-to-date. The more recent booklet by Hirschlaff, useful as it is, does not give more than a short survey of the subject.

It is not within the scope of this book to fill the gap. As the subtitle implies, it treats luminescence specifically for its possibilities in practical application. Thus the photoluminescence of gases and vapors is not included, although from the theoretical point of view this would be one of the most important chapters. It seemed advisable to omit the electroluminescence of gases and vapors as well, since the problems of the discharge of electricity through gases are too manifold and are comprehensively treated in books concerned exclusively with them.

The luminescence of liquids and solids has two main fields of application: analysis and light production, both in the wider sense of the word. In so far as luminescence phenomena can be made useful for any one of these applications, their theoretical background as well as the technique of their

production is discussed in the first part of the book. Rather than enumerate every individual case of application that has ever been published, it seemed that a certain degree of criticism was desirable in the second part. This may serve as an antidote for the over-enthusiasm of those who are inclined to exaggerate the possibilities of such applications, especially in the field of fluorescence analysis.

I was very fortunate to find in the person of Marcel Vogel a younger collaborator who has specialized for several years in the production and application of luminescent paints, and was thus able to supplement my knowledge in a field in which I had but limited experience.

The authors are much indebted to Mr. B. Berry, Dr. H. Popper, Dr. O. W. Richards, and Dr. V. K. Zworykin and to the Bausch and Lomb Optical Co., the Continental Lithograph Corporation, the New Jersey Zinc Co., the Spencer Lens Co., and the R. C. A. Co. who kindly provided photographic prints or cuts for the reproduction of illustrations. It may be pointed out, however, that when the products of a specific manufacturing firm are mentioned no judgment is expressed that similar products of other firms are inferior in quality. It seemed preferable only to give actually existing examples rather than purely schematic descriptions. On the other hand it was, of course, impossible to enumerate every mercury lamp, photometer or microscope manufactured in the United States.

Similarly, the references to publications in scientific or technical journals by no means pretend to be complete. Of several thousand papers only those of special historic importance and the most recent publications have been quoted for every subject, preferentially if they contain a more detailed bibliography. Although some use has been made of the very extensive patent literature, patents have not been referred to.

Finally, the authors want to thank Dr. R. Platzman and Dr. S. L. Simon who helped in correcting the proofs.

PETER PRINGSHEIM

Chicago, July 1943

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PART I

PHYSICS OF LUMINESCENCE

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CHAPTER I

A FEW HISTORICAL REMARKS AS INTRODUCTION

Tales about precious stones shining in the dark stretch back into antiquity. They are supposed to have adorned the temples of the gods and the crowns of princes. This might have been the first technical application of luminescent material. However, the most reliable authors quoted as witnesses for the existence of such fabulous gems do not seem to have committed themselves unambiguously. Aristotle's pupil Theophrastus does not say more than that a carbuncle exposed to sunlight glows like a live coal. And some centuries later Pliny the elder repeats that a flame seems to burn inside of the crystal which he calls anthracite or phlogitis, synonyms of carbuncle. He saw it glitter in the moonlit night, without contending that the "flame" was still visible in complete darkness. More than one minor compiler though, like Diodorus or Volinus, probably misunderstanding his sources or only telling from hearsay, affirms explicitly that a light is hidden in chrysoprase, still another name for the mysterious stone, and that it can be seen during the night like a candle. Aelianus, the poet, knows of a grateful stork which dropped a luminous stone into the lap of a woman at Tarentum as a reward for some kind action. This, of course, does not claim to be scientific information.

The legends and fables of the Near and the Far East are full of such marvelous jewels. From there they return to the fairy tales of medieval Europe. Benvenuto Cellini, a story teller almost as fertile as Scheherazade herself, not only knew many of these tales, but at Ragusa in a merchant's shop, he saw with his own eyes a white sapphire which spread from its interior a sparkle so beautiful and bright that it illuminated a perfectly dark room.[1]

We may ask whether reports of this kind have any connection with the phenomena we call luminescence today, or whether they represent pure products of the imagination. Beyond doubt the ancients knew more than one case of bioluminescence. They could not avoid seeing glowworms and sea fire. Such phenomena as well as the luminosity of rotting wood were treated by Aristotle, who never said a word about luminous stones. Further, it is certain that antiquity and the middle ages were well acquainted with several minerals which are photoluminescent. Most of these, however, show so short an afterglow that it is not perceived without

[1] S. H. Ball, *Sci. Monthly*, **1938.** p. 497; also E. Becquerel, *La Lumière, Ses Causes et Ses Effets*, Paris 1867; H. G. J. Kayser, *Handbuch der Spectroscopie*, Vol. 4, Hirzel, Leipzig 1908.

the help of devices especially designed for the purpose. Luminescence not outlasting the excitation, or fluorescence, is not easily recognized as such. Besides, it would not at all correspond to the description of light emitted in the dark. Certain samples of diamonds and of fluorite, especially the variety called chlorophane, show an afterglow which sometimes persists over an hour and more after the end of excitation by ultraviolet light. It must be kept in mind, though, that no artificial light sources were at hand for the excitation of phosphorescence. The crystal would have had to be exposed to sunlight and then immediately transferred to a dark room. The luminescence would not have lasted through the hours of twilight till after sunset.

The types of luminescence of minerals which might be observed with the greatest probability under normal conditions are the triboluminescence of many diamonds and of different quartz varieties and the thermoluminescence of diamonds, calcites and fluorites. In order to produce the first of these phenomena the crystal must be crushed or at least its surface must be subjected to intense friction. The second is released by a rise of temperature, sometimes only by a few degrees. However, this last experiment can not be performed more than once with a crystal and cannot be repeated without exposing the diamond or fluorspar to an irradiation which was by no means available in old times.

Besides, diamonds are never mentioned in this connection. In at least nine cases out of ten the luminous stone is a "carbuncle," most probably a ruby or in some cases a spinell or a garnet, none of which is phosphorescent. Nor was Cellini's white sapphire a diamond. The famous goldsmith would not make such a mistake in his book on jewelry.

One might, of course, imagine that some Syrian or Egyptian priest anticipated by a few thousand years the feat of that cobbler from Bologna who at last discovered the luminous stone. But this is pure romancing. Not even Herodotus, who knew of every rumor from Asia and Egypt, ever heard of anything of the kind. The column of transparent emerald which he saw in a temple at Tyrus owed its luminosity, beyond doubt, to some artful trickery rather than to a scientific achievement of the priests of Heracles.

Hence, we are justified in beginning the history of phosphorescence with the bootmaker Vincencio Casciarola, who in his leisure hours was an adept of alchemy. In the vicinity of his native Bologna he found some heavy stones and took them home. He hoped to extract from them gold or at least silver. The atom smasher of those days was a furnace and a pair of bellows. After calcination, the stones were not converted into the precious metal hoped for but they had acquired the ability to emit a reddish light for a considerable time after having been insolated. This happened

about 1600. The first names given to the miraculous material were manifold. Stone of Bologna, moonstone, light sponge, and lucifer may be mentioned as a few examples. However, towards the middle of the 17th century the designation "phosphor"* was generally accepted. At present, we know that the stone found by Casciarola consisted, in the main, of barium sulfate which probably contained traces of Bi or Mn and was partially converted into sulfide by the heat treatment. It took more than two and a half centuries before this was understood.

Until then numerous methods were published for the most efficient preparation of the phosphorescent matter without knowing the essential conditions and still less the underlying physical mechanisms. Even nowadays a perusal of the most modern formulae and patents for the manufacture of phosphorescent paints gives the impression that the alchemistic origins are not yet quite outgrown.

In the middle of the 19th century Edward Becquerel laid the foundation for a really scientific treatment of the phenomena.[2] He measured the wave-length of the exciting light and of the emitted light, the duration of the afterglow, the influence of the temperature and many other features. He did not confine his work to the one type of phosphors, but treated the luminescence of many other materials, the uranyl salts, ruby and diamond, fluorite and calcite, etc. It was left to Verneuil[3] and after him, to Lenard,[4] to find in the last years of the 19th century, that nearly all these "mineral phosphors" such as sulfides, oxides, selenides or carbonates owe their luminescence to the presence of impurities like Cu, Mn, Ag, and that only by the use of perfectly pure chemicals is one able to reproduce at will phosphors of different qualities.

At about the same period Crooks[5] and Goldstein[6] started the investigation of luminescence excited by cathode rays.

Fluorescence had been observed perhaps even earlier than phosphorescence in aqueous extracts from an exotic wood "lignum nephriticum" used in pharmaceutics. Other solutions were found later which showed the

* This means light bearer and is the Greek translation of the older "lucifer." The name was given to the stone of Bologna some time before Kunkel discovered the element, phosphorus, which also owes its name to its ability to glow in the dark. The light emission by phosphorus is a case of chemiluminescence, due to an oxidation process.

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[2] E. Becquerel, *Ann. chim. phys.*, **22,** 244 (1848); **55,** 5 (1859); **57,** 40 (1859).

[3] A. Verneuil, *Compt. rend.*, **103,** 600 (1886).

[4] P. Lenard and V. Klatt, *Ann. Physik*, **15,** 225 (1904); also P. Lenard, F. Schmidt and R. Tomaschek, *Phosphoreszenz und Fluoreszenz*, Akademische Verlagsgesellschaft, Leipzig 1928.

[5] W. Crooks, *Proc. Roy. Soc. London*, **32,** 206 (1881).

[6] E. Goldstein, *Wien. Ber.*, **80, II,** 151 (1876).

phenomenon. However, scientists from the Italian doctor, Nicolo Monardes, who was the first to mention it in 1570, to Boyle, Newton, and Hook, and even to F. Herschel[7] and Brewster[8] in the first decades of the 19th century, were all of the opinion that it was nothing but diffusion or dispersion of the incident radiation. Designations like internal dispersion or epipolic dispersion are characteristic of this conception. The main impediment to a better understanding was the necessity of observing the secondary radiation while the primary light beam was passing through the medium.

In 1852 Stokes[9] proved finally that in this case, as in phosphorescence, the irradiated matter becomes self-luminous, and that the wave-length of the emitted light need not be contained in the spectrum of the incident beam. He chose the new name of "fluorescence" for the phenomenon because it is shown with outstanding brilliancy by certain varieties of fluorspar. Further developments of the theory of luminescence are given in the second chapter.

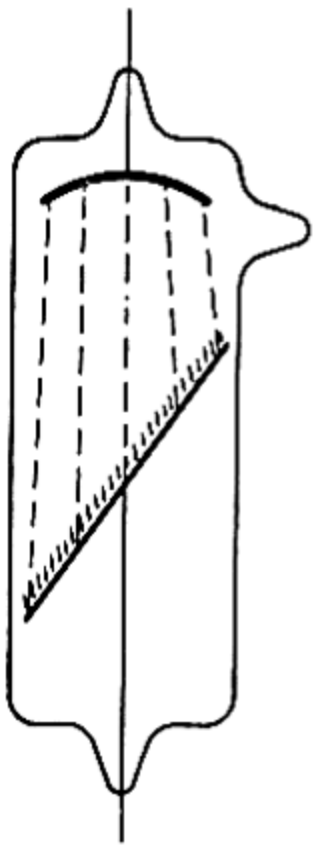

Fig. 1—Old cathode ray fluorescent lamp (after Puluy).

Luminescence began to play a rather important part in the technique of scientific research in the last decades of the 19th century. Fluorescent screens were used in ultraviolet spectroscopy: cathode rays and canal rays were investigated with their help. Fluorescence of such a screen led to the discovery of x-rays and more indirectly of radioactivity as well. Cathodoluminescence was the most important method by which Crooks,[10] Boisbaudran,[11] and others succeeded in discovering and ultimately separating the rare earth metals. This series of papers beginning in 1880 provided the first example in which luminescence was applied to chemical analysis.

It took much longer before any important applications of luminescence were found useful outside of the research laboratories of pure science. It is true that as early as 1625 a man called Peter Poterius made little animals from phosphorescent material "which were a very lovely sight at night." The manufacture of such phosphorescent "novelties" has become a fast growing industry lately. However, it is also true that little more than

[7] J. Herschel, *Phil. Trans.*, **1845**, p. 143.
[8] D. Brewster, *Phil. Mag.*, **32**, 401 (1848).
[9] G. Stokes, *Phil. Trans.*, **143, II**, 463 (1852).
[10] W. Crooks, *Proc. Roy. Soc. London*, **35**, 262 (1883).
[11] Lecoq de Boisbaudran, *Compt. rend.*, **100**, 1437 (1885).

ten years ago it was asserted in an article in "Handbuch der Physik" that fluorescent lamps had no future for illumination.[12] They were considered to be inefficient. This was probably correct for the only type of fluorescent tubes then existing. In these, for instance in one constructed by Puluy, which may be found in many collections of apparatus in old laboratories, luminescence was excited by cathode rays impinging on a fluorescent screen (Fig. 1). Before the modern fluorescent lamp could be invented the hot cathode gas discharge tube had to be developed. The ever increasing number of fields in which luminescence is applied to practical purposes forms the main content of the second part of this book.

[12] P. Pringsheim, *Lumineszenzlichtquellen* (*Handbuch der Physik XIX*). Springer, Berlin 1928.

CHAPTER II

THEORETICAL BACKGROUND

1. Nature of Light

Classical theory records that light consists of electromagnetic waves propagated with a velocity which in empty space has the value $c = 3 \times 10^{10}$ cm. per second or 300,000 km. per second. Its intensity is defined by the amplitude of the waves. Its quality, the property which is responsible for the sensation of color in our vision, is correlated with the wave-length λ or the frequency ν. Wave-length and frequency are related by the equation $\nu = \frac{c}{\lambda}$. In modern physics the wave number $\tilde{\nu} = \frac{1}{\lambda}$ is used more frequently than ν.

The wave-length of light is measured in Ångstrom units: 1 Å = 1/100,000,000 = 1×10^{-8} cm., the corresponding wave number is measured in cm. $^{-1}\left(\frac{1}{\text{cm.}}\right)$. Visible light, which has a spectrum extending from red to violet with wave-lengths of 8000 to 4000 Ångstroms or 12,500 to 25,000 cm.$^{-1}$, forms only a small part of the total electromagnetic spectrum. This latter extends on one extreme to radio waves with wave-lengths of several miles and on the other to the gamma rays emitted by radioactive substances and even further to certain components of cosmic radiation with $\lambda = 10^{-15}$ cm.

The problems which are treated in this book concern only the middle part of the electromagnetic spectrum, *i.e.*, visible light and ultraviolet radiation. The latter may be conveniently subdivided into the near U.V. (4000–3000 Å), the far U.V. (3000–2000 Å), and the "Schumann U.V." (2000–1200 Å). All these kinds of radiation may be classified as light (which, of course, in the ordinary sense of the word, means only visible light). In so far as x-rays are used to produce luminescence they must also be taken into account. They are "light" of wave-lengths from about 100 Å to 0.01 Å. The shorter their wave-length, the "harder" and the more penetrating are the x-rays. Infrared radiation, immediately adjoining the long wave-length end of the visible part of the spectrum, will occasionally be mentioned in connection with fluorescence and phosphorescence processes.

A light emission spectrum as actually observed may consist of isolated bright lines separated from each other by dark intervals. It can consist of one or more broad structureless bands,* or it can cover continuously the

* This purely phenomenological description is not intended to be sufficient to distinguish between line and band spectra in the spectroscopic sense.

whole region from the red to the U.V. without any pronounced selectivity.

An absorption spectrum is produced when light with a continuous spectrum is passed through a medium which absorbs only part of the light. Absorption spectra consist of dark lines or dark bands on a luminous background.

Since the quantum theory was introduced by Planck and Einstein we know that, though the wave character of light with all its consequences has to be maintained, the energy which is carried by these waves has a corpuscular nature. Light is composed of units called quanta or photons, each photon having an energy $E = h\nu$; h, a universal constant (Planck's constant), has the value 6.63×10^{-27} erg sec. If a molecule absorbs light of a frequency ν, it cannot absorb any quantity of such light; it can just absorb one photon, $E_\nu = h\nu$, and conversely it cannot emit more or less than one photon of this frequency. If it emits radiation of a smaller energy, this radiation has also a smaller frequency ν', so that again $E' = h\nu'$.

Niels Bohr developed this principle further by introducing the assumption that a molecule can exist only in certain energy states, and that it cannot contain or absorb any arbitrary amount of energy. The lowest of the states of a molecule is the "ground state" E_0. States of higher energy $E_1, E_2, \ldots$ are called excited states. The transition of the molecule from a lower energy level E_i to a higher level E_k requires an energy influx $\Delta E = E_k - E_i$, which may be provided by the absorption of a photon $h\nu_{ki} = E_k - E_i$. The inverse passage $E_k \rightarrow E_i$ can be accompanied by the emission of light of the same frequency $\nu_{ik} = \nu_{ki}$ (Fig. 2). In both cases the energy ΔE may also be provided or lost by some other process, for instance by a collision.

The internal energy of a monatomic molecule is defined exclusively by the configuration of its electrons. The corresponding energy levels of the atom are in general separated from each other by relatively large intervals, so that the transitions between levels determine widely separated lines in the visible or ultraviolet part of the spectrum corresponding to large $h\nu$-values. In diatomic and polyatomic molecules energy is also contained in the vibrations of the atomic nuclei relative to their center of gravity, and in the rotation of the molecule around the main axis of inertia. The spacings between the corresponding energy levels which are superimposed upon the electronic levels are much narrower than those between the electronic levels themselves. Thus a great many lines are accumulated within a narrow spectral region forming a so-called band system (Fig. 3).

Since a molecule has only discrete energy levels $E_0, E_1, E_2 \ldots$, it is able to absorb or emit only light of certain discrete frequencies ν_{ik} ($i = 0, 1, 2 \ldots k = 1, 2, 3 \ldots, i < k$).

At moderate temperatures practically all molecules are in the electronic ground state E_0, although some of the molecules may contain one or even two vibrational quanta. Hence the absorption spectra show in general only the frequencies ν_{0k}.

In isolated single molecules, *e.g.*, in gases of low pressure, the energy states are very sharply defined and transitions between them produce narrow and sharp lines. In more complicated molecules, especially in condensed systems (in liquids or solids), the narrowly spaced energy levels become more or less broadened and frequently overlap. Accordingly the

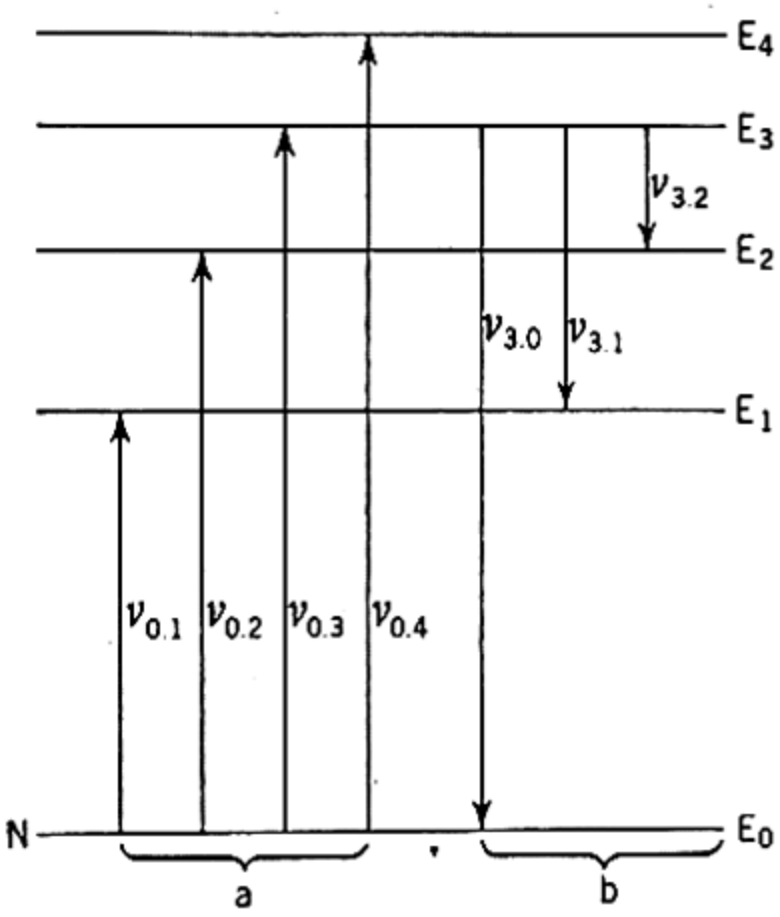

Fig. 2.—Energy levels of an atom.
a: Absorption lines from the ground state.
b: Emission lines from electronic state E_3.

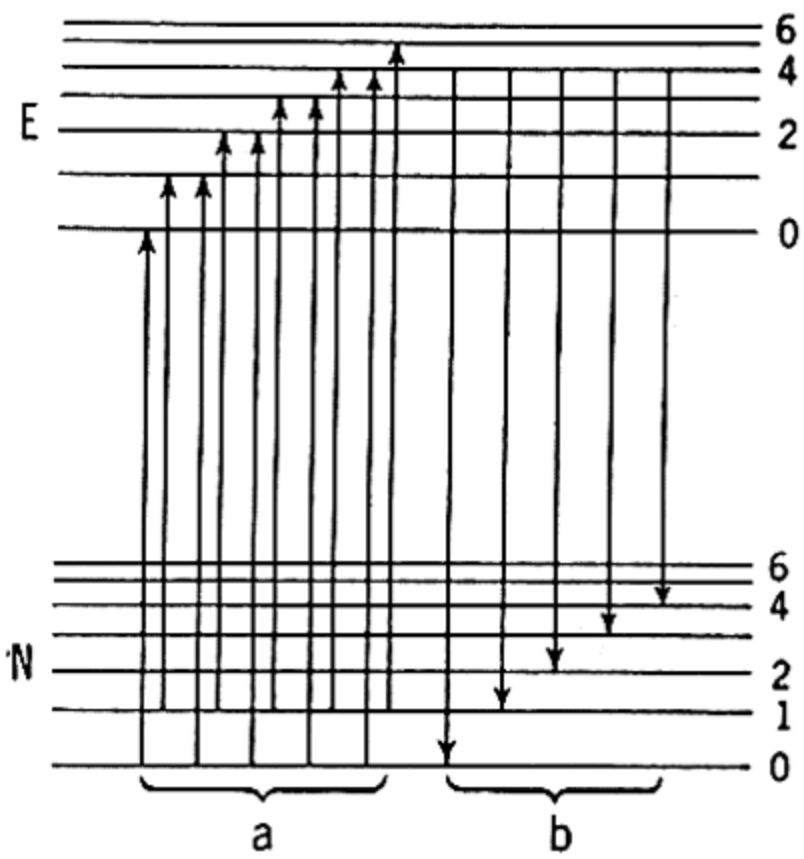

Fig. 3.—Two electronic energy states of a molecule with superimposed vibrational levels.
a: Absorption series from the two lowest vibrational levels.
b: Emission series from one excited level.

absorption and emission spectra consist of more or less broad and diffuse bands (Fig. 4).

If a molecule is raised into an excited state E_k by light absorption or any other kind of mechanism and if, apart from the ground state N(with the energy E_0) several other energy levels E', E'' . . . . are situated below E_k, the emission spectrum will result from transitions from E_k to all or to some of the levels E_0, E', E''. . . . The levels E', E'' . . . . can either correspond to different electronic excitation states (as in Fig. 2) or they can be due to the superposition of different vibrational energies on one and the same electronic state (as in Fig. 3). The emission spectrum originating from one single excited state will thus consist of a series of lines. In more

complicated molecules, and especially in condensed systems, sequences of broad bands will appear instead, and eventually these will merge into one continuous band showing several peaks of higher intensity.

The transition probabilities between different energy levels $E_i \rightarrow E_k$ of one and the same molecule may be of quite different orders of magnitude. Great transition probabilities correspond to strong absorption and emission lines or bands, small probabilities to weak lines or bands. If the transition

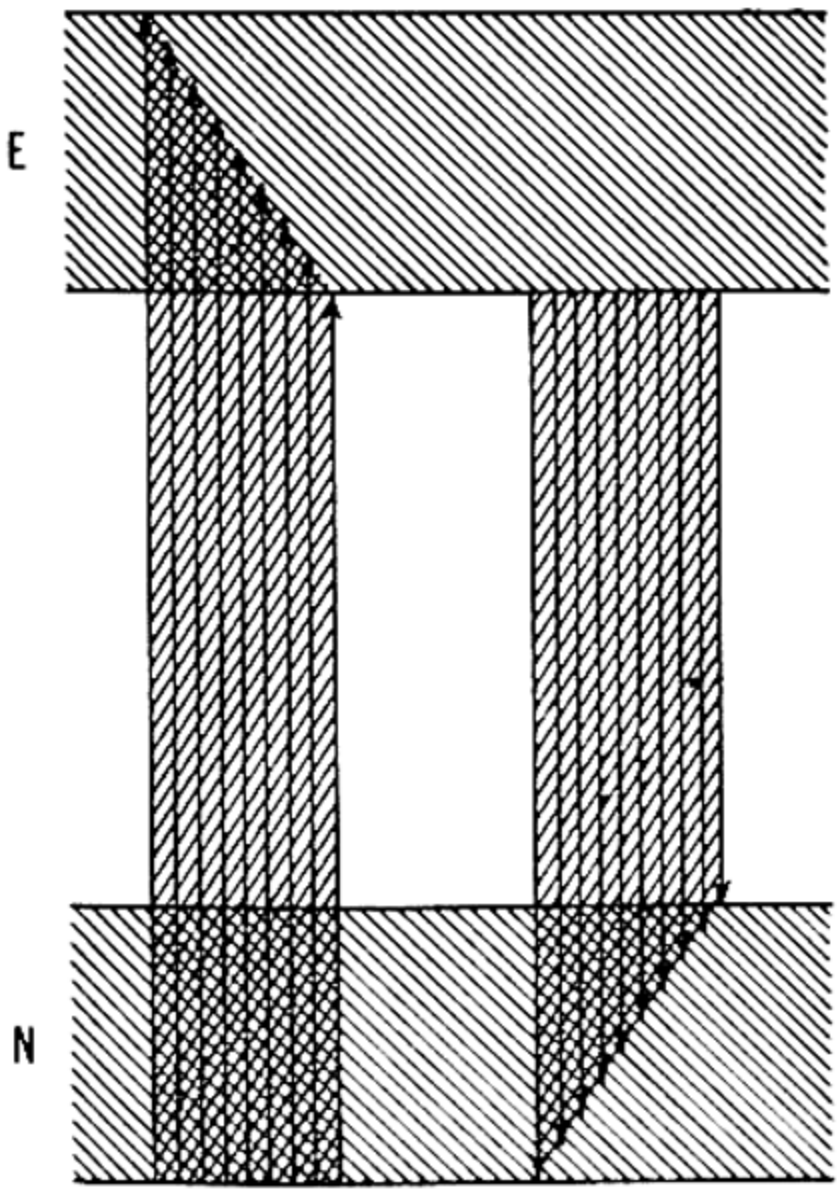

Fig. 4.—Two electronic states of a molecule giving origin to the absorption or emission of a broad band.

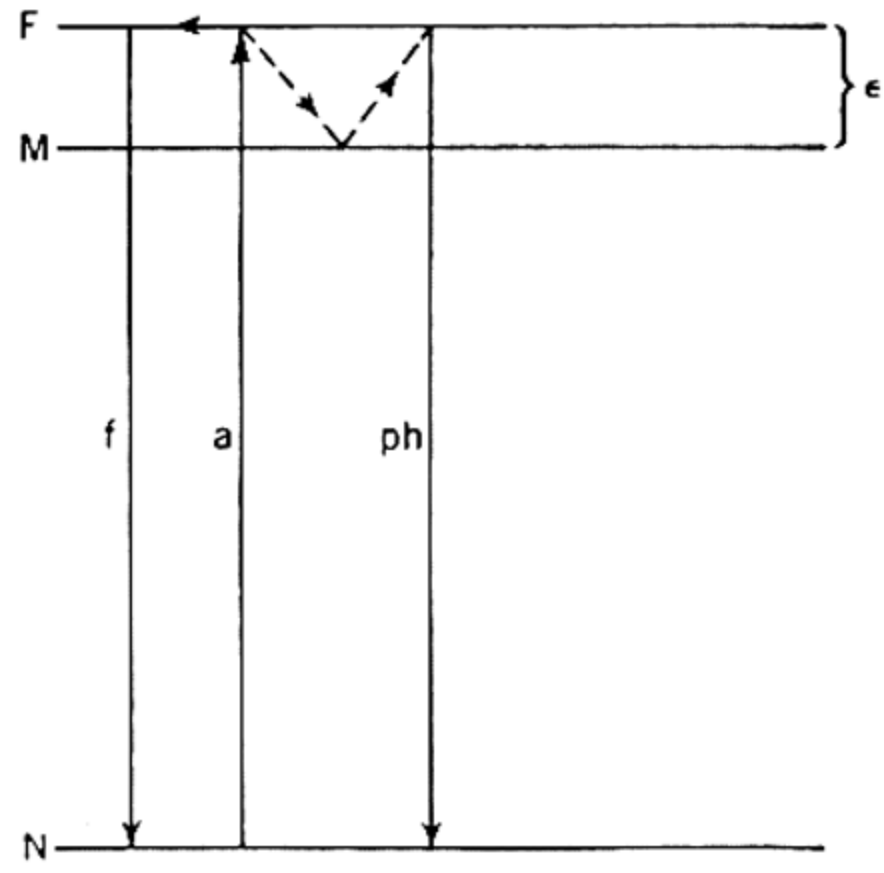

Fig. 5.—Energy levels for the production of phosphorescence.
a: Absorption process.
f: Fluorescence process.
ph: Phosphorescence process.

probability is extremely small, the transmission is called "forbidden." An excited state is called metastable or quasistable, if the transitions from this state to the ground state or any other state of lower energy are all forbidden (compare Fig. 5).

The time during which a molecule remains in an excited state before it returns spontaneously, with light emission, to a lower state, is called the lifetime of the excited state. For atoms and many molecules these lifetimes can be calculated by the application of so-called selection rules. For "allowed" transitions corresponding to lines in the visible part of the

spectrum the lifetime is of the order of 10^{-8} sec., while for transitions forbidden by selection rules it almost never exceeds a few seconds.* An excited state is "metastable" if selection rules make all transitions to lower levels impossible. In polyatomic molecules or in crystals, states of high energy can exist, in which the configuration of the atomic nuclei is altered. The probability of a spontaneous transition from such a state into the normal nuclear configuration, which is characteristic of the ground state, can be exceedingly small and thus the lifetime of such a "quasistable state" may last hours or even years.

It is perhaps not superfluous to emphasize, for the sake of the reader not used to physical terminology, that more or less doubtful "modern" hypotheses are not implied when light emission and absorption are represented by transitions between different energy levels in a molecule. This representation is based only on two assumptions, and these are as solidly established as any part of classical physics. The first one is that the spectra of simple molecules in the vapor state consist of narrow sharp lines characteristic of the molecules, and the second is, that light of a wave-length λ is absorbed and emitted in quanta of energy $h \times c/\lambda$.

2. Luminescence

Since light is a form of energy, energy must be supplied to every material system serving as a source of light. In the greatest number of cases this is done by heating the system. When the thermal agitation of all molecules within the system is increased, then simultaneously more and more of the molecules are raised into excited states. The higher the temperature, the greater the number of excited molecules and the greater the intensity of the emitted light. To such thermal excitation we owe not only the light radiated by the sun, but also the light produced by most of our artificial devices, from the torch and the oil lamp to the Welsbach mantel and the tungsten filament bulb.

It is possible, however, to transfer energy only to those parts of the molecules which are responsible for light emission. The molecules can be brought into excited states without increasing their average kinetic energy or without heating the system. For light emitted under such conditions, E. Wiedemann has introduced the term luminescence.[1]

A rather frequent misstatement asserts that if an emission spectrum differs widely from that of a glowing filament by its intensity distribution or its selectivity it is due to luminescence. Such laws as Wien's law or

* For the sake of completeness it may be mentioned that certain metastable states of simple atoms, *e.g.*, the state $6\ ^3P_0$ of the even mercury isotopes should have an infinite lifetime according to the theoretical selection rules.

[1] E. Wiedemann, *Ann. Physik*, **37**, 177 (1889).

Planck's law determine black body radiation in contradistinction to the radiation of any other heated body, but they afford no possibility of discrimination between thermal radiation and luminescence. The emission spectrum of an europium salt or of sodium vapor at high temperatures may consist of a few narrow bands or a single spectral line, but such an emission is thermal radiation nevertheless. The only characteristic feature of *luminescence* is that it does not obey Kirchhoff's law. If the intensity of the emitted light exceeds the intensity of the radiation of the same wavelength from a black body of the same temperature, the radiation is a case of luminescence.*

Luminescence can be either fluorescence or phosphorescence. According to the original definition *fluorescence* is a light emission which does not continue a measurable time after the end of the excitation process. *Phosphorescence* persists when the excitation is discontinued. Sometimes the emission lasts for many hours. This definition of fluorescence and phosphorescence is still found in many modern publications, and in a general way and for most practical purposes, it can be admitted to be true. It must be understood, however, that in some cases typical fluorescence can show an afterglow observable even without any special instrument, while on the other hand the duration of phosphorescence may become very short at higher temperatures.

Fluorescence is due to the spontaneous transition of a molecule from an excited state to a lower energy level. The mean life of this process depends only on the transition probability; it is in most cases very short, with $\tau \leq 10^{-7}$ sec. and practically never exceeds 1 sec. Furthermore, it is practically independent of temperature.[2] The characteristic feature of *phosphorescence* is that a fraction of the excited molecules does not immediately begin to emit light by returning from the excited state F (see Fig. 5) to the ground state G, but passes instead into a metastable or quasistable state M, of somewhat smaller energy than F. From M the molecules

* This statement of Kirchhoff's law will cover almost every practical case, although it is not quite complete. Radiation of some light sources may have less intensity than black body radiation of the same temperature and be luminescence nevertheless, if the radiating body absorbs very little of the radiation which it emits. If $E_{\lambda T}$ and $A_{\lambda T}$ are the emissive and absorptive power of the light source for wavelength λ and temperature T, and, if $E^0_{\lambda T}$ is the emissive power of the black body, $A^0_{\lambda T}$ being equal to unity, then luminescence is defined by the inequality $\frac{E_{\lambda T}}{A_{\lambda T}} > E^0_{\lambda T}$.

If for instance hydrogen gas in a transparent quartz tube is heated to 1000° C., it will remain perfectly transparent, A being very small, and it will emit no light; the emission of the red hydrogen line may be excited by a very weak electric discharge and cause *luminescence*. The red radiation from a black body at 1000° C. might be a hundred times stronger.

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[2] G. R. Fonda, *J. Applied Phys.*, **10**, 408 (1939).

can only return to F with subsequent light emission accompanying the passage $F - G$ when the missing energy $\epsilon = F - M$ is restored to them by the heat movement of the surrounding medium.[3] This return occurs within a short time at high temperatures. It might be delayed a good deal at low temperatures. At very low temperatures the phosphorescence may be completely "frozen in." The molecules then remain in their quasistable state M, until, by a rise of temperature, the "trapped" radiation is again released. The smaller the energy difference between F and M, the lower the temperature necessary for "freezing in" the phosphorescence. With high values of ϵ, phosphorescence may even be frozen in at room temperature. This is the origin of all so-called *thermoluminescence.*

A third kind of luminescence process does not fit into these definitions of fluorescence or phosphorescence and may be called recombination afterglow. It plays a rather important part in the luminescence of certain mineral phosphors. It occurs when electrons are completely removed from their original molecules by the absorption of light. Light emission results when these electrons recombine with any one of the excited molecules. While normal fluorescence and phosphorescence are monomolecular reactions, recombination afterglow is a typical bimolecular reaction, its intensity being proportional to the square of the number of excited centers. The duration of the afterglow is usually short and does not exceed fractions of a second,[4] as long as the electrons are not "trapped" during their movement across the crystal lattice. In the latter case the phenomenon may appear as a superposition of a monomolecular and a bimolecular process with one or the other of the two prevailing. When the exciting radiation is cut off, a "monomolecular" process decays according to an exponential law

$$I = I_0 e^{-at}$$

where I_0 is the initial intensity, $a = 1/\tau$ the transition probability and τ the mean life period of the excited state. The decay of a recombination luminescence follows a hyperbolic law

$$I = I_0/(1 + bI_0 t)$$

The most characteristic difference between the two types of decay curves is not their shape, but their dependence on the value of I_0 and on the temperature T. The exponential curve is quite independent of the initial intensity, while the steepness of the curve increases with increasing temperature. For the hyperbolic type the slope is little influenced by tempera-

[3] F. Perrin, *Compt. rend.*, **182**, 219 and 929 (1926); S. I. Vavilov, *Physik. Z. Sowjetunion*, **5**, 369 (1934).

[4] W. De Groot, *Physica*, **6**, 275 (1939).

ture but becomes much steeper with increasing initial intensity (Fig. 6). The validity of the exponential law for fluorescence of very short duration ($t = 10^{-7}$ *sec.*) has not yet been proved, but it has been ascertained for

a b

Fig. 6.—Growth and decay of luminescence at different primary intensities (De Groot).

a: ZnS (hyperbolic law). b: Canary glass (exponential law).

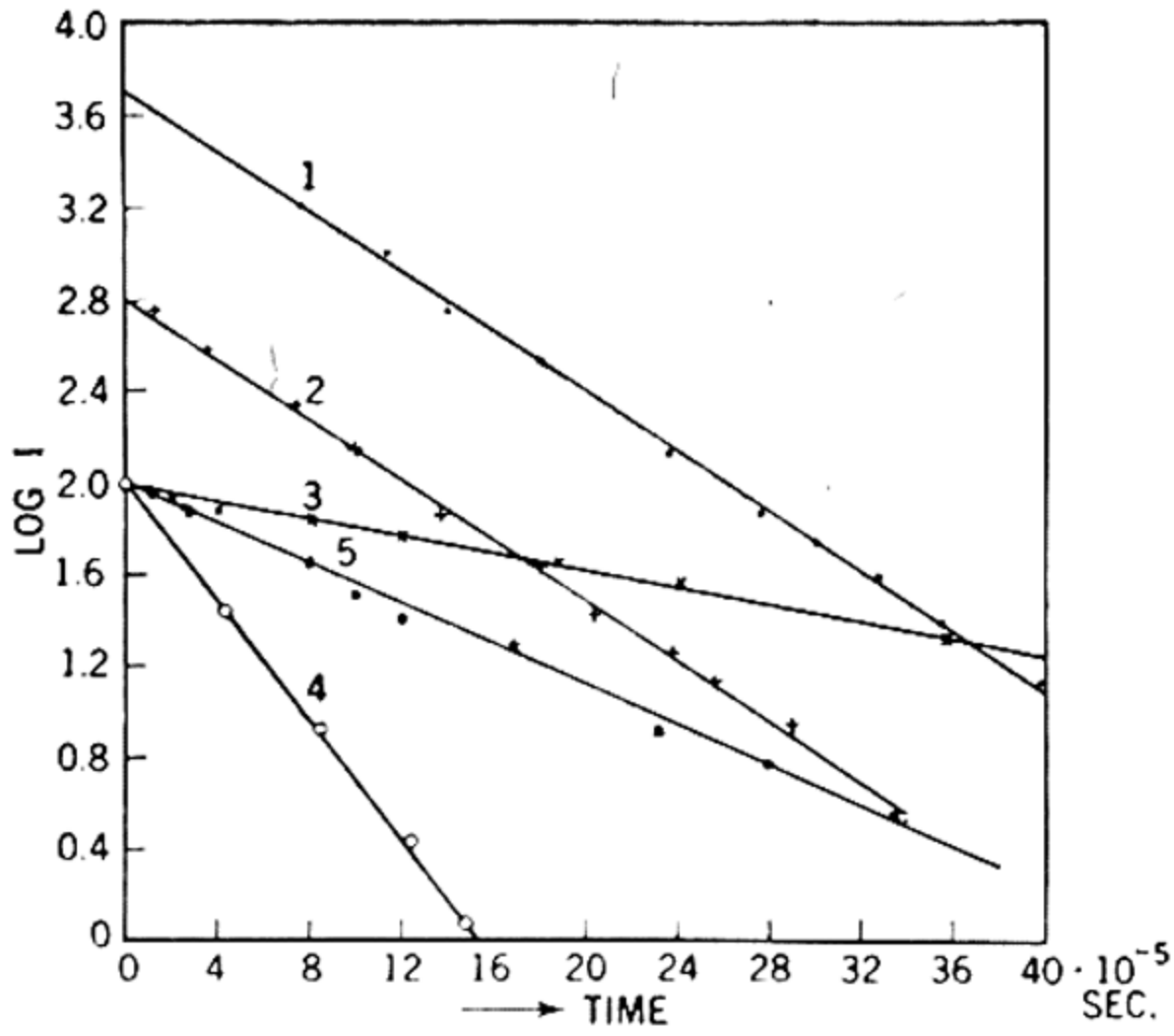

Fig. 7.—Logarithmic decay curves for slow fluorescence of uranyl salts (Vavilov and Levshin).

1: Uranyl rubidium sulfate, intensity of exciting light = 10.
2: Same, intensity of exciting light = 0.1.
3: Uranyl sulfate.
4: Uranyl ammonium carbonate (1–4 in crystalline state).
5: Uranyl sulfate in H_2SO_4. 0.35 g. per cc.

some cases of slower fluorescence (uranyl salts, canary glass, certain dyestuffs in solid solutions, ruby) (Fig. 7).[4,5] Since most synthetic phosphors

[4] S. I. Vavilov and V. L. Levshin, *Z. Physik*, **48**, 397 (1928); P. Pringsheim and H. Vogels, *J. chim. phys.*, **36**, 345 (1936); also G. N. Lewis and Th. T Magel, *J. Am Chem. Soc.*, **63**, 3005 (1941).

are available only as microcrystalline powders, an exact confirmation of any decay law can hardly be expected for such a phosphor. The individual grains need not have identical properties, and in the case of bimolecular reaction, the intensity of the primary irradiation differs for the grains at different depth within the powder. But the interdependence of the slope of the decay curve and initial intensity shows that the luminescence processes of short duration in these phosphors are monomolecular in some cases and bimolecular in others.[6] Real phosphorescence, due to "electron trapping" with strong temperature dependence, should probably always have a strictly exponential decay. In a few cases in which a single crystal could be tested, this proved to be true (Fig. 8).[7] In general, the decay

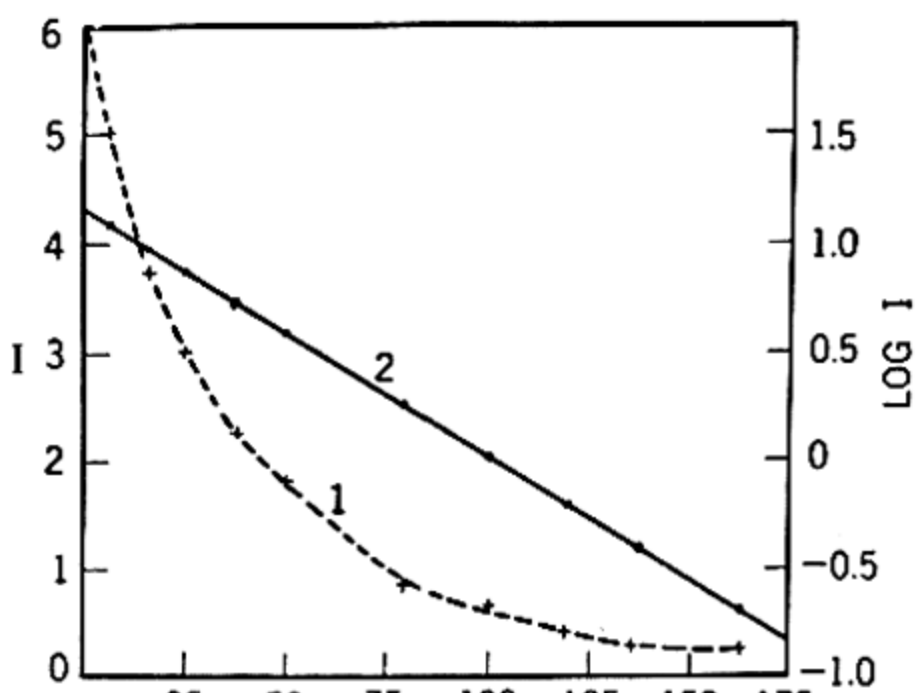

Fig. 8.—Decay curves for a single crystal KCl (Tl) phosphor (Buenger and Flexig).
1: Intensity as function of time. 2: Log intensity as function of time.

curves, sometimes lasting over several days, can best be represented by a superposition of several exponential curves (*cf.* page ix, *A* 6).

With regard to the mode of excitation there are, for practical applications, only two really important types of luminescence: photoluminescence, produced by the absorption of light, to which the terms fluorescence and phosphorescence are in general applied without further qualification, and electroluminescence, which is produced by the impacts of electrically charged particles, such as electrons (cathode rays or β-rays) or ions such as α-rays or canal rays. Chemiluminescence, resulting from certain chemical reactions, is rather interesting in itself, but not of great importance for the subjects treated in this book. The light emission of hot flames, as in a Bunsen flame containing sodium, is not chemiluminescence but thermal emission.[8]

[6] R. P. Johnson, *J. Optical Soc. Am.*, **29**, 387 (1939).
[7] W. Buenger and W. Flexig, *Z. Physik*, **67**, 42 (1931).
[8] H. Kohn, *Physik. Z.*, **15**, 98 (1914).

Most books list a whole series of other types of luminescence: thermoluminescence, bioluminescence, triboluminescence, crystalloluminescence, sonoluminescence, and others. The first of these is nothing else than phosphorescence, excited previously by light absorption, radioactive radiation, etc., and "frozen in" at room temperature. It is not produced, but only released, by heating. Bioluminescence is a special form of chemiluminescence accompanying certain biological processes.[9] The mechanism of triboluminescence, which appears at its best when certain crystals are crushed, is not too clearly understood; probably it is a tertiary effect due to the production of minute electrical discharges. The same may be true for some of the other luminescent processes mentioned above.

3. Excitation of Luminescence

In order to excite photoluminescence, light must be absorbed. Since light is absorbed and re-emitted in quanta of energy $h\nu$, and since no more energy can be emitted by the individual molecule than it has absorbed, luminescence can have no greater frequency or shorter wave-length than the exciting light. The light emitted may be of smaller frequency or greater wave-length if the total amount of absorbed energy is not given out in the emission process. In condensed systems, *i.e.*, liquids or solids, this condition will even be the rule, since the excited molecules are apt to transfer at least that part of the absorbed energy which is contained in the oscillation of the nuclei to neighboring molecules in the form of heat motion before the light emission takes place (compare Fig. 4). A law found empirically by Stokes[10] states that fluorescent light always has a greater wave-length than the exciting light and its corresponding absorption bands. This law was explained by Einstein on the basis of quantum theory.[11] Small transgressions of Stokes' law are possible, if at higher temperatures heat energy is transferred from the surrounding molecules to the fluorescing molecule during the time it stays in the excited state.

A substance perfectly transparent to visible light can never be excited to luminescence under the action of visible light. It can, however, emit visible fluorescence when excited by an ultraviolet radiation which it can absorb. In general any photoluminescent substance has an absorption band in the spectral region immediately adjoining the short-wave limit of the luminescence band and even somewhat overlapping it. This follows from the energy level scheme of Fig. 4. Hence red fluorescence is excited by orange light, yellow by green, green by blue, and violet by ultraviolet. Infrared fluorescence, observed in a few cases such as chlorophyll and some

[9] E. Harvey, *Living Light.* Princeton Univ. Press, Princeton 1940.
[10] G. Stokes, *Phil. Trans.*, **143,** 463 (1852).
[11] A. Einstein, *Ann. Physik*, **17,** 132 (1905).

crystal phosphors,[12] can be excited by red light. Most photoluminescent substances have further absorption bands at shorter wave-lengths, that is, in the ultraviolet region. With very few exceptions the same fluorescence that is excited by light absorption in the long wave-length absorption band can also be excited by light of shorter wave-lengths[13] (Fig. 9). The fluorescence intensity radiated by a substance varies with the wave-length of the exciting light only in so far as the absorption power is a function of the wave-length. So-called specific excitation spectra are, in general, nothing but the characteristic absorption spectra of the photoluminescent substance.[14]

The absorption of x-rays is a function of the atomic number, or atomic weight, of the absorbing atoms. It is exceedingly small in the light atoms

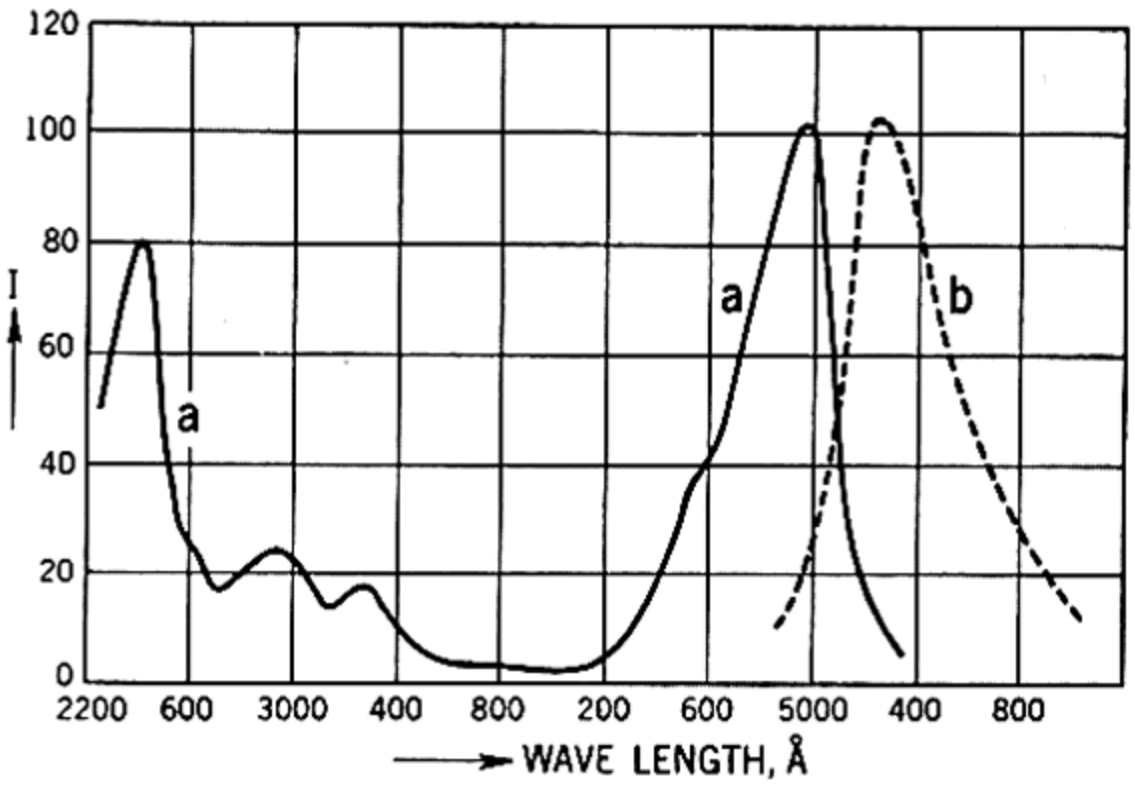

Fig. 9.—Absorption and fluorescence bands of fluorescein in alkaline solution.
a: Absorption bands. b: Fluorescence bands.

of which most organic substances consist. Only luminescent materials containing heavy atoms will emit bright fluorescence under x-ray excitation.* When fluorescence is excited by x-rays, the luminescence is actually

* According to Lenard's way of representing history, x-rays were not discovered by Lenard because he used a fluorescent screen made of some aromatic ketone in his cathode ray experiments. Roentgen tried to repeat some of these experiments but could not get hold of one of the ketone screens and took instead a barium platinocyanide screen, which became luminescent under the impact of the then unknown radiation. And thus it happened that the rays are universally called Roentgen rays—only Lenard prefers to call them not Lenard rays, but high frequency rays.

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[12] E. W. Pauli, *Ann. Physik*, **34**, 739 (1911); Ch. Dhéré and O. Biermacher, *Compt. rend.*, **203**, 412 (1936).

[13] A. Jabloński, *Compt. rend. soc. polon. phys.*, **7**, 1 (1926); S. Szczeniowski, *ibid.*, **8** 60 (1927).

[14] E. Nichols and E. Merritt, *Phys. Rev.*, **11**, 381 (1910); S. I. Vavilov, *Phil. Mag.*, **43**, 307 (1922); E. J. Bowen, *Proc. Roy. Soc. London*, **154**, 349 (1936).

a tertiary effect produced by secondary cathode rays set free by the x-rays.

In cathodoluminescence, the most important case of electroluminescence, the primary energy is supplied by electrons which have acquired a high velocity under the action of an electrical field. The energy of an electron after a free fall through an accelerating potential of one volt is called an electron volt (*e.v.*) $1\ e.v. = 1.6 \times 10^{-12}$ erg or 1.6×10^{-19} watt sec. In order to excite a molecule from the ground state E_0 to an energy level E_1 so that it may be able to emit radiation of frequency ν, the energy of the electron must be at least equal to $h\nu = \frac{hc}{\lambda}$. The wave-length corresponding to the energy of one e.v. is 12395 Å. This "Franck-Hertz law"[15] is analogous to Stokes' law in photoluminescence and plays an important part in the study of the electroluminescence of gases. These problems, however, imply a complete treatment of electrical discharges through gases and are beyond the scope of our book. Though the discharge of electricity through a gas produces luminescence radiation itself, gas discharge lamps will be mentioned here only as light sources used for the production of luminescence in other substances.

In the cathodoluminescence of solids the Franck-Hertz law hardly needs to be taken into account because in all practical cases the voltage applied is much larger than the minimum voltage required to provide the excitation energy.

Of minor importance for technical application is the electroluminescence produced by ions in canal rays. It has not been used for any other purposes than the study of the charged ions themselves in the so-called mass spectrographs. The same is true for the excitation of luminescence by β- or γ-rays of radioactive substances. However, fluorescence excited by α-particles, doubly ionized helium atoms emitted by radioactive substances, finds a widespread use in self-luminous paints. Here, as well as in the case of x-ray excitation, the primary rays excite the luminescent centers not directly but by means of secondary cathode rays.

4. Efficiency and Intensity

In all cases where luminescence is used as a light source, the question of economy becomes important. There are three different ways of defining the efficiency of a luminescent source of light: the luminous efficiency, the energy efficiency, and the quantum efficiency. Of these the first has greatest importance from the technical point of view, the last is most important from the theoretical point of view.

A. The luminous efficiency is the ratio of the total light output to the

[15] J. Franck and G. Hertz, *Verhandl. deut. phys. Ges.*, **15**, 613 (1913).

total energy input without questioning which part of this energy is absorbed by the luminescent material or lost by reflection, transmission, or by any other process. The primary energy per second is usually given in watts or ergs/sec. The light output is not defined in a real energy unit but in lumens. The number of lumens present in the radiation is the resultant of three components: the total energy of the emitted light, its spectral

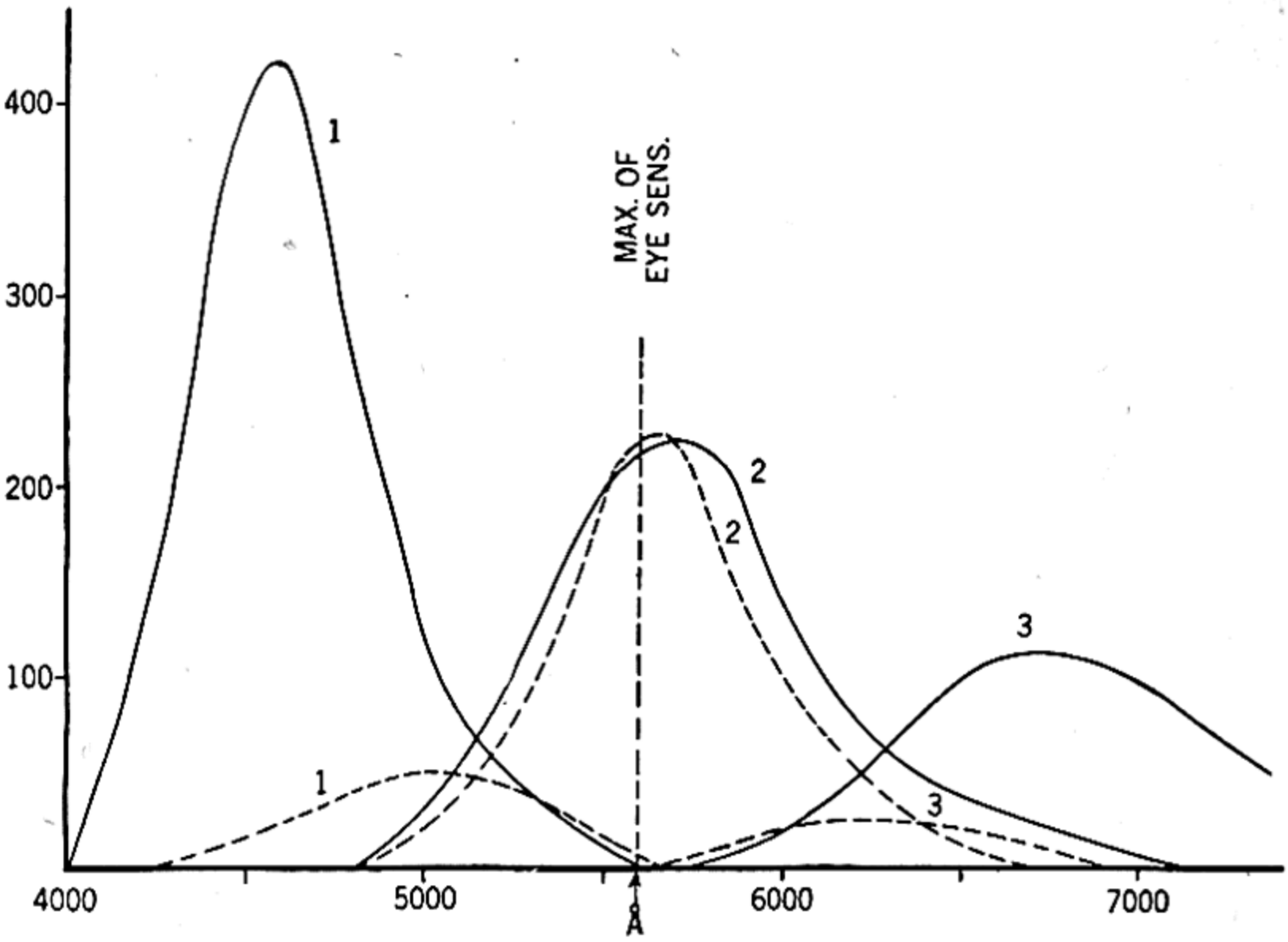

Fig. 10.—Spectral energy distribution and visibility curve for three phosphors (Leverenz).

——— energy distribution
- - - - - visibility
} of fluorescence band.

1. ZnS(80%) CdS(20%) Ag(10^{-4})
2. ZnS(50%) CdS(50%) Ag(10^{-4})
3. ZnS(20%) CdS(80%) Ag(10^{-4})

distribution, and the sensitivity curve of the human eye (Fig. 10, also Fig. 53, page 140).

An amount of energy emitted in the green or yellow part of the spectrum corresponds to a much greater number of lumens than the same amount of energy if the light is red or violet. Infrared or ultraviolet light does not contribute at all to the luminous efficiency. If all primary energy were transformed into light of 5550 Å, maximum of the eye sensitivity curve, the highest luminous efficiency obtainable would be 621 lumens per watt.

Table 1 gives under the heading Å the wave-lengths of the visible

spectrum in Ångstrom units, under I the relative intensities in the spectrum of daylight corresponding to these wave-lengths, under V their relative visibility,* and under $I \times V$ the relative contribution of each wave-length to the total visible light output. Taking into account only those wave-lengths for which the visibility exceeds 2% from 6800 to 4400 Å, a light source whose emission spectrum could be matched exactly to daylight, with no energy in the extreme red or violet part of the spectrum, would have only 42% of the maximum luminous efficiency. One watt input produces 621 lumens of pure green radiation but only 261 lumens of daylight.

It must be kept in mind that daylight, white light, and almost every colored light are purely subjective concepts (Fig. 10). White light can be

TABLE I

RELATIVE INTENSITY I AND VISIBILITY V OF DAYLIGHT RADIATION IN DIFFERENT SPECTRAL REGIONS[16]

Å	I	V	$I \times V$	Å	I	V	$I \times V$
7200	75	0.001	0.075	5600	98	1.00	98
7000	79	0.004	0.31	5400	99	0.95	94
6800	83	0.02	1.66	5200	99	0.71	70
6600	87	0.06	5.22	5000	100	0.32	32
6400	89	0.18	16.0	4800	97	0.14	13.5
6200	92	0.38	35.0	4600	90	0.06	5.4
6000	94	0.63	59.0	4400	76	0.023	1.5
5800	96	0.87	83.5	4200	65	0.004	0.26
				4000		0.0004	

obtained by very different combinations of colored lights, for instance by the superposition of two complementary spectral colors. Table II gives three examples of such combinations: E_1 and E_2 are the relative intensities; L_1 and L_2 are the relative luminosities; λ_1 and λ_2 are the wave-lengths of the two components.[17] A lamp emitting any one of these superposed radiations would appear white to the eye and so would a white screen illuminated by the lamp. Colored objects, however, would by no means show their characteristic "body colors" as in real daylight. They would, instead, reflect exclusively the two colors contained in the spectrum of the lamp or appear black. In order to avoid this effect the "white light"

* These data refer only to cone vision (photopic vision) at normal brightnesses above 1 millilambert. For very low brightness compare page 139.

[16] *Natl. Bur. of Standards U. S. Misc. Pub.*, **114**, 16; *J. Optical Soc. Am.*, **30**, 55 (1940).

[17] H. W. Leverenz, *J. Optical Soc. Am.*, **30**, 309 (1940).

must have a spectral composition as close as possible to that of the "daylight" of Table I. This fact is important not only for the problem of white light illumination, but also for television in natural colors (compare page 149).

In the case of photoluminescence it would be illogical to measure the influx of primary radiation in lumens since the visibility of the exciting radiation is in no way connected with its exciting power. The number of lumens contributed by ultraviolet light would always be zero. For this reason the introduction of a new intensity unit for near ultraviolet radiation producing luminescence has been proposed.[18] This unit, called a "fluoren," would be defined as the quantity of radiation of wave-length 3650 Å producing a defined luminescence intensity on a standard luminescent screen, *e.g.*, a certain kind of canary glass. The application of the unit would, of course, be limited to the excitation of fluorescence by light of this one

TABLE II[17]

PRODUCTION OF WHITE LIGHT BY SUPERPOSITION OF TWO MONOCHROMATIC RADIATIONS OF INTENSITIES E_1 AND E_2, OF RELATIVE LUMINOSITIES L_1 AND L_2, AND OF WAVE-LENGTHS λ_1 AND λ_2

λ_1	λ_2	E_1	E_2	L_1	L_2	Lumens per watt	Per cent efficiency
4590 (blue)	5720 (yellow-green)	39.5	60.5	3.9	96.1	366	58.9
4775 (green-blue)	5765 (yellow)	49.5	50.5	12.3	87.7	323	51.7
4900 (blue-green)	5910 (orange)	65.3	34.7	32.9	67.1	249	39.5

wave-length, since the efficiency of ultraviolet light in producing luminescence may vary with its wave-length.* Since this "fluoren," however, must be determined by laboratory measurements involving fractions of a watt, it would apparently be much simpler to retain the watt or milliwatt itself as the unit of luminescence exciting power. This procedure is not only equally applicable to light of every wave-length, but it is in agreement with the definition of luminous efficiency for every other kind of light production, which is always measured in lumens per watt.

B. The energy yield Φ is the ratio of the energy of the luminescent light, in ergs or watt seconds, to the energy absorbed by the luminescent

* Though for many purposes fluorescence is usually excited by black light lamps with the wave-length 3650 Å, the great importance of short wave-length excitation by the mercury resonance line and even the neon resonance lines must be taken into account.

[18] J. O. Kraehnbuehl and H. J. Chanan, *Trans. Illum. Eng.*, Soc., **36**, 151 (1941).

material, not accounting for the part of the primary energy reflected or transmitted.*

C. The quantum yield Q is the ratio of the number of photons contained in the emitted light to the number of photons absorbed by the luminescent material.

One absorbed photon never produces more than one excited molecule. Since the energy of the individual photon increases proportionally to its frequency, it follows that even when $Q = 1$, the energy yield Φ is in general smaller than 1. For:

$$\Phi = \frac{\lambda_a}{\lambda_e} Q$$

where λ_a and λ_e are the wave-lengths of absorbed and emitted light respectively.† From the viewpoint of economy in photoluminescence it is therefore desirable that the ratio λ_a/λ_e be not too small, or that the wave-length of the exciting light be not too far down in the ultraviolet part of the spectrum.

The total energy emitted by an incandescent body can be calculated from the intensity emitted in a given direction by means of Lambert's cosine law. According to this law the intrinsic intensity of a surface remains constant when it is foreshortened by being viewed at an oblique angle. Lambert's law has to be replaced by Lommel's law for the light emission from a smooth surface of a transparent fluorescent solid or liquid like canary glass or an aqueous aesculin solution. In this case the intrinsic intensity increases rapidly with increasing angle of observation. If the fluorescence is viewed "backwards," from the side of the impinging primary radiation, this effect is to a large part obscured by the total reflection of the fluorescent light at the boundary between glass or liquid and air, and the function which connects the intensity and the angle of observation becomes very complicated.[13] The same is true if the fluorescent body is more or less turbid and has a rough surface, as is the case for phosphorescent paints. For such a paint the intrinsic intensity, compared to the brightness observed in a direction perpendicular to the surface, is larger than it would be if calculated from Lambert's law, up to an angle of 60°. At larger angles it falls rapidly below the Lambert law value. Thus the total energy

* Although this is the correct definition of the yield, it is at times not easy to find the necessary data; then the yield is measured by the ratio of emitted to impinging energy (instead of absorbed energy).

† Only in the practically uninteresting case of resonance radiation, when $\lambda_a = \lambda_e$, are Φ and Q identical.

[13] R. W. Wood, *Phil. Mag.*, **117**, 82 (1906); F. Lommel, *Ann. Physik*, **10**, 449 (1880).

emitted over the half sphere is almost exactly the same as that from an incandescent body which has the same brightness when viewed perpendicularly.[20] If Lommel's law were valid, the total intensity would be four times as large under these conditions. For a transparent fluorescent lacquer some intermediate law probably has to be applied. At any rate it is not safe to calculate the total intensity emitted by a fluorescent body from measurements made under some specific angle without having ascertained the real angular distribution of intensities in this special case.

The number of excited molecules is always small compared to the total number of unexcited molecules when the duration of luminescence is short, as in all cases of normal fluorescence, in most cases of recombination afterglow and even in some kinds of short-lived phosphorescence. Under these circumstances the luminescence intensity is proportional to the intensity of the primary radiation up to the highest values.* However, if the yield of a recombination afterglow is well below 100% because of the presence of some quenching mechanism like the transfer of the absorbed energy into heat, and if this second effect does not depend on the square of the number of excited centers, then the luminescence intensity will increase more than proportionally with the intensity of the exciting light. Riehl observed this behavior with silver activated zinc sulfide phosphors, for which the luminescence yield was nearly doubled when the primary light intensity was increased from 1 to 400. Similar, but smaller effects of the same kind were obtained with other ZnS phosphors, especially at higher temperatures, where the thermal quenching by internal conversion becomes stronger. According to Riehl this phenomenon may be of some importance for the light production in commercial fluorescent lamps. On the other hand a saturation of excitation is reached after a definite absorption of primary energy in the case of phosphorescence of slow decay. This saturation is apparently due to the complete filling of all electron traps or quasistable levels.† The phosphor, as far as its afterglow is concerned, cannot be excited beyond this state. Since there is only a certain maximum energy stored up in the phosphor, only this energy can be re-emitted. The stronger the initial intensity of the afterglow, the sooner the whole energy will be spent. Very long afterglow and very great brightness are two qualities which cannot be found in the same phosphor.

* An exception, which is observed for cathode ray excitation, is explained on page 29.

† In general the "electron traps" are much less numerous than the molecules able to absorb exciting radiation in a phosphor. Thus only the phosphorescence of the phosphor is saturated, while its fluorescence may be increased farther.

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[20] M. Schilling, *Z. tech. Physik*, **31**, 750 (1941).

A phosphor can be fully excited or "saturated" in the same way by a strong primary source of radiation within a short period of time or by a weaker primary source in a correspondingly longer time. The maximum "light sum" stored in the phosphor will be always the same. As a rule the longer the full excitation by a given primary light source takes, the slower the phosphorescence decays after the end of the excitation.*

Even if the fluorescence yield does not depend on the concentration of luminescent molecules or luminescent centers, the intensity† of the light emitted by the unit volume, or by the unit surface, must be a function of this concentration. At low concentrations the absorption of the exciting radiation is weak. Hence I will be small, and in a transparent liquid or solid solution, it will be very nearly constant along the primary beam. At higher concentrations the distance to which the exciting radiation penetrates becomes shorter. The depth of the luminescent layer contracts closer and closer to the surface, and, though the intensity of light emitted by the smallest volumes close to the surface may still increase, the total light output, when observed from the side whence the primary radiation impinges, will remain constant.

The hypothesis, however, that Q should be independent of the concentration c, seems almost never to hold true for the fluorescence of liquid solutions or for the activated mineral phosphors. In most cases the yield is constant only at the very lowest concentrations.[21] It decreases, slowly at first, then rather sharply with increasing concentration. The theoretical reason for this very general law is not yet well understood, but its practical consequence is an intensity curve that shows a very pronounced maximum

* Compare page 136.

† In photometry the term "intensity" is used for point light sources only. For two-dimensional surfaces the term "brightness" is employed. For the total emission of a three-dimensional volume no special terminology has been introduced. The use of the term "brightness," if it is measured in lamberts (with the dimension of lumens per cm.^{2} per steradian), assumes the validity of Lambert's cosine law. Since this law states that brightness is independent of the angle of observation, it is advisable to avoid it in connection with measurement of fluorescence intensities. Intensity as used here is defined as the total energy radiated per unit volume.

As a matter of fact, photometry does not determine directly either the brightness or intensity of a light source, but rather the illumination of the photometer surface. From this value, the geometric ratios, and the knowledge of the directional (angular) distribution of the radiation from the light source, the total intensity emitted by a luminescent volume can be derived. This intensity, divided by the energy absorbed in the same volume, is the efficiency.

Table III, p. 27, may prove useful for the conversion of the different units used in original papers for the definition of intensity or brightness.

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[21] S. I. Vavilov, *Z. Physik*, **31**, 750 (1925).

at a given concentration, the so-called optimum concentration* (Figs. 11 and 12).

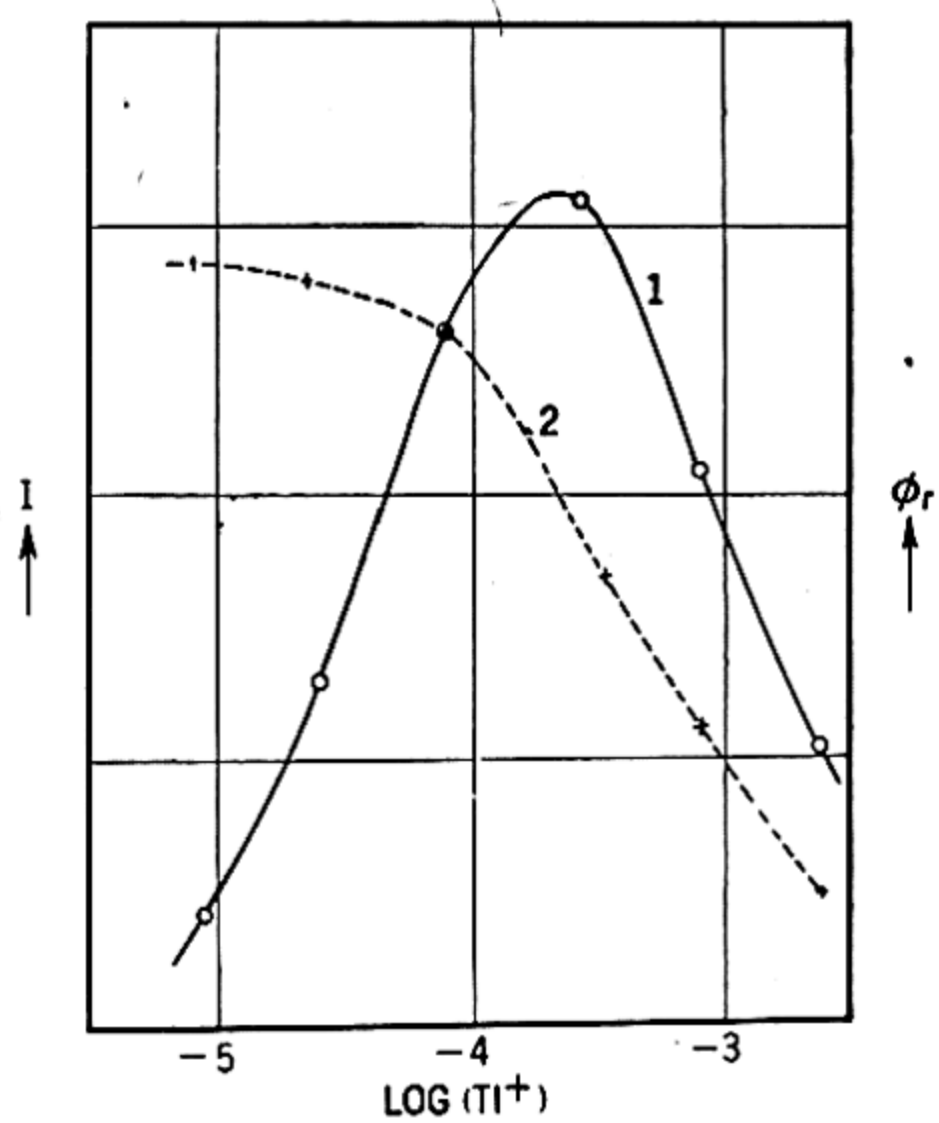

Fig. 11.—Fluorescence intensity and fluorescence yield of a KCl-TlCl solution as a function of TlCl concentration.

1: Apparent intensity I. 2: Relative fluorescence yield Φ_r (Pringsheim and Vogels)

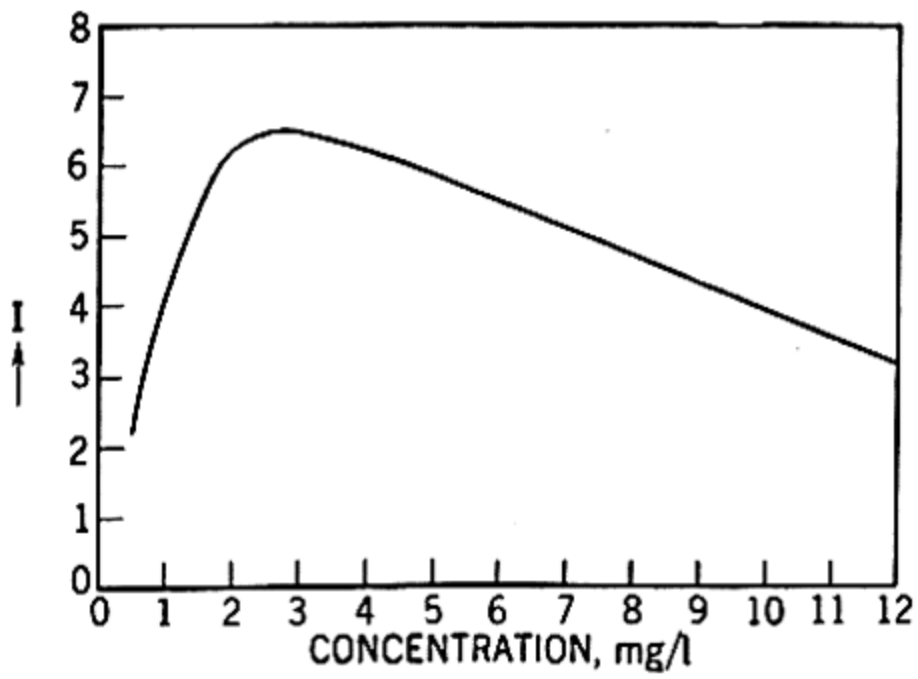

Fig. 12.—Apparent fluorescence intensity of riboflavin as function of concentration (Karrer and Fritsche).

* The phenomenon is easily observed by comparing the fluorescence of two dyestuff solutions, one saturated and the other diluted 100 times. The results of this experiment cannot be simply explained by the fact that the exciting radiation penetrates less with increasing concentration and consequently fails to activate the deeper layers in the solution.

For a given material the quantum yield of photoluminescence Q is in general independent of the wave-length of the primary light over a large

TABLE III

CONVERSION OF PHOTOMETRIC UNITS

	Foot-candles	Lumens per sq. cm.	Milli-lamberts	Foot-lamberts	Candles per Sq. ft.	Candles per Sq. in.	Candles per Sq. cm.
Foot-candles....	1[a]	= 0.001076	= 0.269	= 0.25	= 0.0796 $=\frac{1}{4}\pi$	= 0.00055	= 0.0000857
Lumens per sq. cm.....	929	= 1	= 25.0	= 23.2	= 7.4	= 0.0514	= 0.00796
Milli-lamberts...	3.716	= 0.004	= 1	= 0.929	= 0.295	= 0.00205	= 0.000318
Foot-lamberts...	4	= 0.00435	= 1.076	= 1	= 0.318 $=1/\pi$	= 0.00221	= 0.000342
Candles per sq. ft.	12.56 $=4\pi$	= 0.0137	= 3.38	= 3.142 $=\pi$	= 1	= 0.00694	= 0.00108
Candles per sq. in.	1808	= 1.97	= 487	= 452	= 144	= 1	= 0.155
Candles per sq. cm.	11664	= 12.66	= 3142	= 2916	= 929	= 6.451	= 1

[a] 1 foot-candle = 1 lumen per square foot = $\frac{1}{4}$ candle per square foot. 1 *HK* (Hefner candle) = 0.9 international candles.

spectral range. Q remains constant as long as the exciting radiation has a wave-length shorter than the peak of the last absorption band.[22] For exciting light of greater wave-lengths the quantum yield decreases rapidly† (Fig. 13). The quantum yield is strongly influenced by external conditions such as temperature, nature of the solvent, presence of quenching

† This behavior cannot be explained by a reference to the energy level scheme of Fig. 4. Absorption of long wave-length light may be very improbable because it can only occur in molecules of high vibrational energy in the electronic ground state N. But if a molecule is raised by such an absorption process into the electronic excited state E_1, it has exactly the same chance to emit a light quantum as any other excited molecule. However, the extension of the absorption band towards greater wave-lengths may be due to another reason, the perturbation of the energy states of the absorbing molecule by the action of solvent molecules. If these perturbations persist over a sufficient period of time after the excitation, the probability of a conversion of the absorbed energy into heat is larger for these excited molecules than for others. Hence their fluorescence yield is smaller.

[22] S. I. Vavilov, *Z. Physik*, **42**, 311 (1927); G. R. Harrison and P. A. Leighton, *Phys. Rev.*, **38**, 899 (1931); also E. J. Bowen, *Proc. Roy. Soc. London*, **154**, 349 (1936).

substances, and so on. The color of the luminescent light of different materials is in no way connected with the absolute values of Q. The yield can be high or low for a blue fluorescence as well as for a red fluorescence. Q varies between extremely wide limits, *i.e.*, from 100% to less than 1%, even for similar substances under like external conditions. Table IV gives some examples; none of the values claims great accuracy.

TABLE IV

QUANTUM YIELD OF PHOTOLUMINESCENCE

Liquid solutions are at room temperature

Substance	Solvent	Color of fluorescence	Q
Uranin[23]	Alcohol	Green yellow	70
Uranin[23]	Water	Green yellow	84
Eosin[23]	Water	Yellow	16
Erythrosin[23]	Water	Orange	2
Rubrene[24]	Benzene	Red	≈100
Anthracene[24]	Benzene	Blue	29
Benzene[24]	Hexane	U.V.	11
Fluorene[24]	Hexane	U.V.	≈100
Methylene blue[25]	Alcohol	Red	<2
Anthracene[24]	Pure crystal	Violet	≈100
Napthacene[24]	Pure crystal	Yellow	4
Napthacene[24]	Dissolved in anthracene	Yellow green	≈100
Ethioporphyrin[25]	Ether	Red	1
Rhodamine B[26]	Cellulose acetate	Red	62
Rhodamine B[26]	Gelatin	Red	21
$K_2Pt(CN)_4^*$ [27]	Water	Green	4–5
KTlCl[28]	Crystals	U.V. and blue	80
ZnS(Cu) or (Ag)[29]	Crystals	Green (blue)	≈100
Zn_2SiO_4 (Mn)[29]	Crystals	Green	25†–70
$ZnBeSiO_4$ (Mn)[30,31]	Crystals	Orange	25–55
$CdSiO_3$ [30]	Crystals	Pink yellow	55
$CaWO_4$ [30]	Crystals	Blue	70
CdB_2O_4 [30]	Crystals	Pink	66

* At −21°C. in alcohol, Q = 21 per cent.

† Under excitation by the Ne resonance lines, Q = 25 per cent.

[23] S. I. Vavilov, *Z. Physik*, **22**, 266 (1924).

[24] E. J. Bowen and A. H. Williams, *Trans. Faraday Soc.*, **35**, 765 (1939).

[25] H. Hellstroem, *Arkiv Kemi, Miner. Geol. Stockholm*, **A12**, 23 (1937).

[26] G. R. Fonda, *J. Optical Soc. Am.*, **26**, 316 (1936).

[27] J. A. Khvostikov, *Physik. Z. Sowjetunion*, **9**, 210 (1936).

[28] W. Buenger, Z. *Physik*, **66**, 711 (1938).

[29] N. Riehl, *Ann. Physik*, **29**, 636 (1937).

[30] R. N. Thayer and B. T. Barnes, *J. Optical Soc. Am.*, **29**, 131 (1939).

[31] A. Ruettenauer, *Z. tech. Physik*, **19**, 148 (1938).

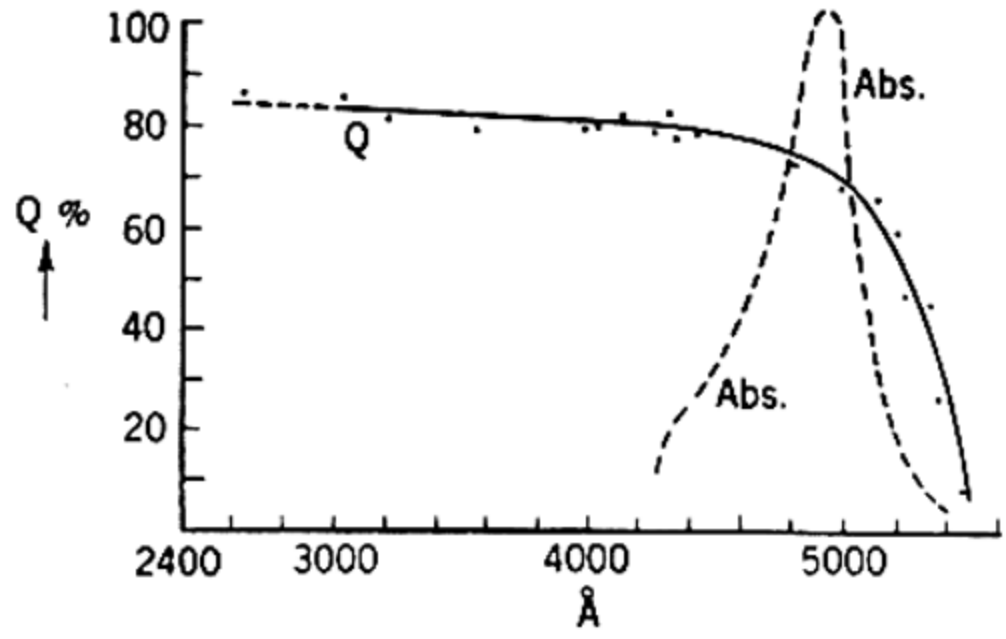

Fig. 13.—Quantum yield of a fluorescein solution in water (Vavilov).

In photoluminescence the energy of the primary radiation is defined by the number of photons per sq. cm. and by their frequency; in cathodoluminescence the corresponding factors are the current density and the kinetic energy of the individual electrons, the latter depending on applied voltage (V). While a photon, whatever its frequency, can only transfer its energy to one single molecule and so excite it, an electron of great kinetic energy can lose its energy stepwise and excite a great number of molecules. Hence the quantum yield Q has no significance in this case.

For small current densities (i smaller than five microamp. per sq. cm.) and accelerating voltages below 1000 volts the fluorescence brightness of a Willemite screen is proportional to L and V^2:[32]

$$L = \text{const. } iV^2$$

The general law connecting the fluorescence intensity L with i and V has the form:

$$L = f(i)(V - V_0)^n$$

where the "dead voltage" or "threshold voltage" V_0 varies for different phosphors from 0 to several hundred volts; n is a constant that ranges in value from 1 to 3. The function $f(i)$ is independent of V. The curves representing L as a function of i have the same trend for all values of V. For small current densities they are very nearly straight lines and the efficiency Φ is constant (Fig. 14). At higher values of i, L tends towards a maximum or saturation value while Φ decreases.[33] (Fig. 15.) For Willemite the efficiency at 10^{-4} amp/cm^2 is only about 2% of the efficiency at 10^{6} amp. cm.^{2} The value of the current density at which the *fluorescence* yield begins to decrease varies widely for different phosphors. For example, the value for Willemite is about 10^{-6} amp. per sq. cm.; in some zinc sulfide phosphors it is a hundred times as large. The saturation of the

[32] Th. B. Brown, *J. Optical Soc. Am.*, **27**, 180 (1937).
[33] W. B. Nottingham, *J. Applied Phys.*, **10**, 73 (1939).

phosphorescence of the same materials is usually reached at much smaller current densities. The existence of a saturation value for the luminescence

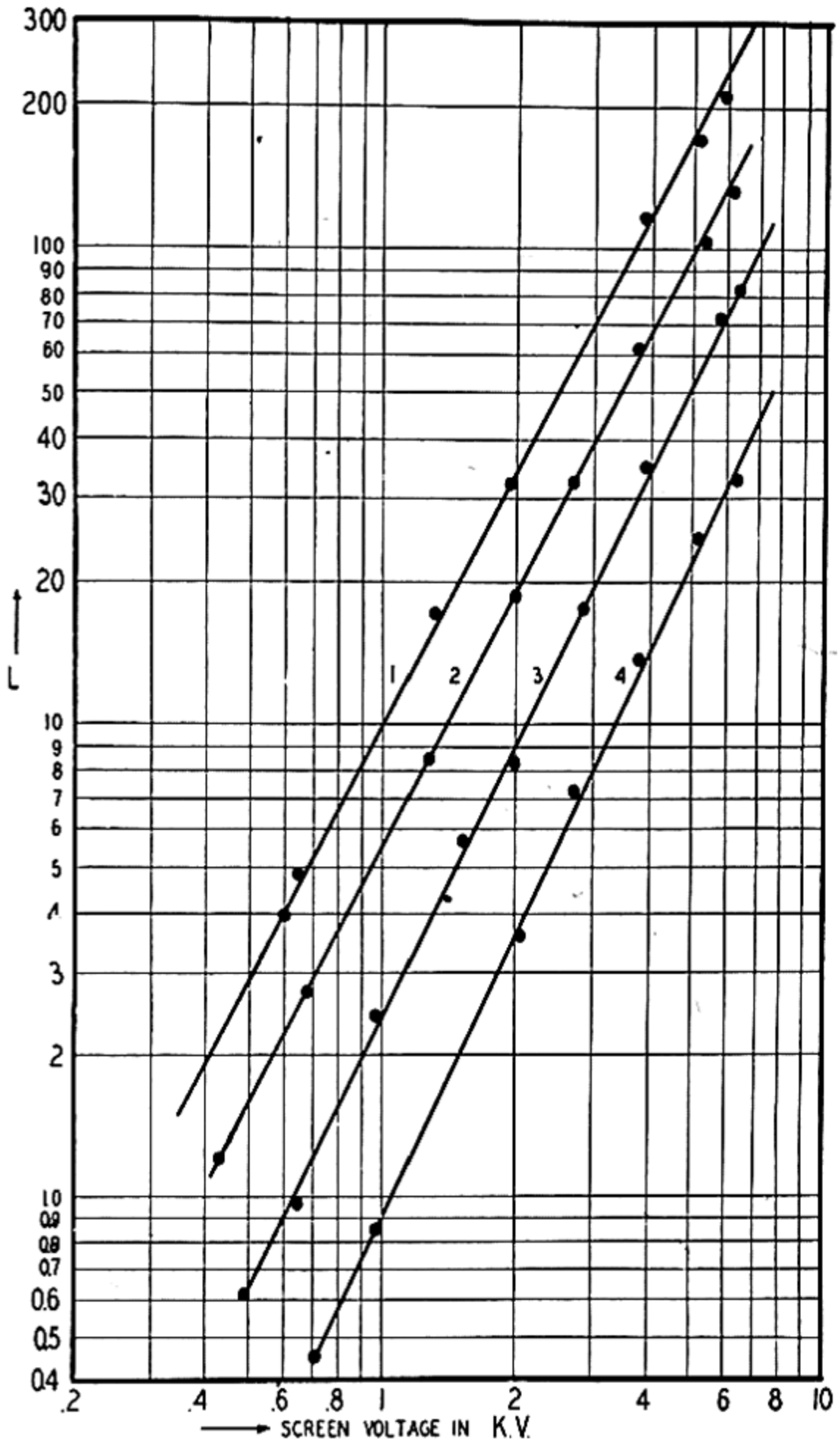

Fig. 14.—Light output L as function of screen potential in cathode luminescence for different current densities (Martin and Headrick).

1: Current density i = 200 amp. per square cm.
2: i = 150 amp. per square cm.
3: i = 50 amp. per square cm.
4: i = 10 amp. per square cm.

yield can be explained in both cases by the same reasoning: when no centers are left unexcited, the luminescence cannot be further increased.

Saturation is reached at a relatively low current density if at least one of three conditions is fulfilled: if there are few luminescent centers, if the probability of the excitation by the single impinging electron is high, or if the mean life of the excited state is long.

For the reasons stated above, the increase of luminescence intensity with increasing voltage has no analogue in photoluminescence. Electrons of higher energy penetrate deeper into the interior of the phosphor and are thus able to excite a greater number of centers along their path.[34] If the luminescence intensity of a zinc sulfide phosphor is enhanced by raising the

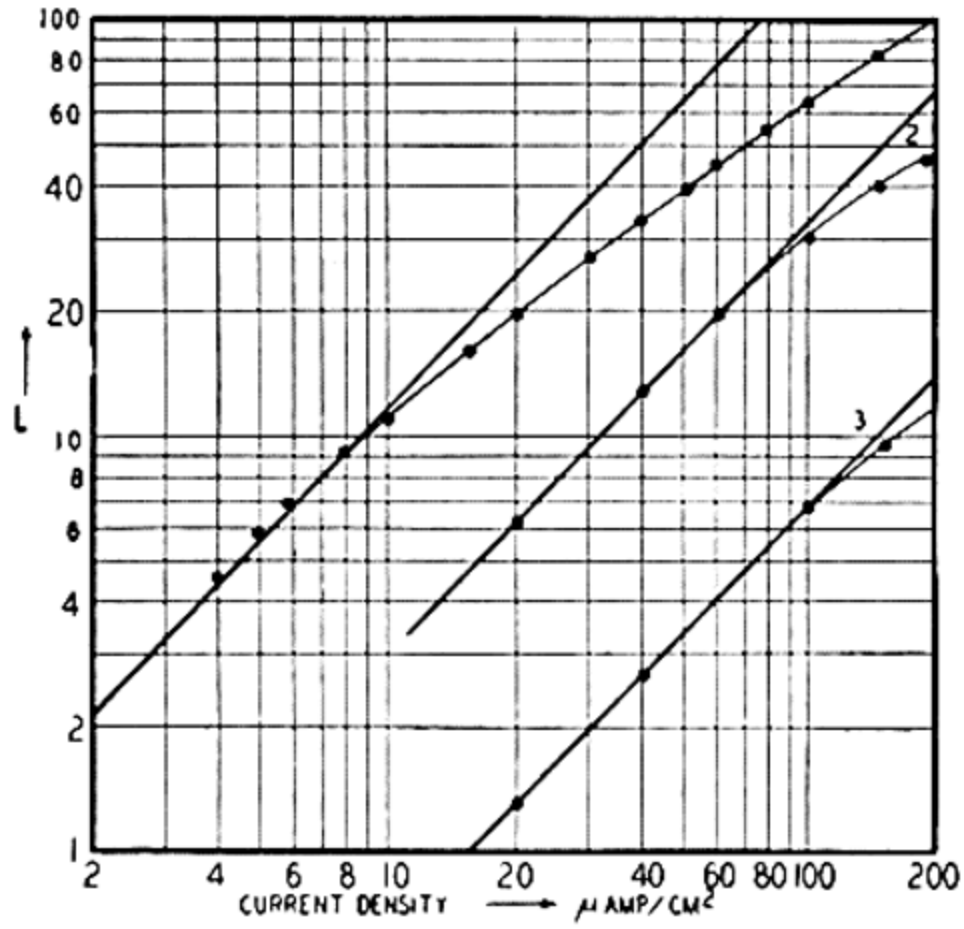

Fig. 15.—Light output L of different phosphors at constant screen voltage of 2000 volts as function of the current density (L in arbitrary units) (Martin and Headrick).

1: Zinc beryllium silicate 2: Zinc sulfide-silver
3: Calcium tungstate.

current density, the slope of the typical hyperbolic (bimolecular) decay curve of the afterglow becomes steeper. If the increase of luminescence intensity is due to a rise of the voltage, the slope of the decay curve remains unaltered. In the first case, the density of the excited centers, their number per unit volume is increased, in the second case; the volume within which centers are excited is enlarged without changing the probability of recombination.

The absolute yield of cathodoluminescence is never very large since a great part of the primary energy is always converted into heat and secondary electron emission. Few measurements of the energy yield are

[34] S. T. Martin and L. B. Headrick, *J. Applied Phys.*, **10**, 1169 (1939).

available, and these do not agree too well with each other. The values depend, to a high degree, on the nature of the screen and on the voltage applied to the tube. On the average the yield is of the order of a few per cent, rarely exceeding 10%.[35] As for the luminous efficiency, a series of results have been published for different screens with the parameters $V = 4000$ volts, $i = 1.25$ microamps. per sq. cm. The efficiencies vary from 0.23 lumens/watt for $CaWO_4$ to 3.5 lumens/watt for ZnS.

The efficiency of luminescence excited by x-rays is of the same order of magnitude.[36] The most recent and most accurate measurements give yields of about 3% for a commercial screen of German manufacture, *Neossal*. The yield is practically independent of the hardness of the x-rays within a range in which the absorption of the rays decreases nearly to one-half (Table V). The wave-length of the light emitted by the screen was 5260 Å. Hence a yield of 3% corresponds to a luminous efficiency of 14.5 lumens per watt. These data refer to the "technically useful" light yield, as observed from the back of the screen. Not only is the light absorption

TABLE V

FLUORESCENCE YIELD OF AN X-RAY SCREEN

Voltage of tube in *kv*	80	100	120	140	160
Absorption in screen	0.40	0.33	0.28	0.24	0.23
Energy yield in per cent	3.2	3.2	2.9	3.0	3.0

within the screen neglected, but also the energy radiated in the opposite direction. Therefore the real efficiency might be three to four times larger.*

Considering the relatively low efficiency of luminescence excited by x- and cathode rays, it is rather astonishing that the luminescence yield of ZnS phosphors under α-ray bombardment is as high as 80% and perhaps even more.[37]

5. Chemical Reactions and Other Phenomena Connected with Luminescence

Many luminescent materials deteriorate more or less rapidly under the action of radiation which excites fluorescence. In general this deterioration is characterized by a decrease of luminescence and some change of

* This probably applies also to some results published for the yield of cathode ray luminescence.

[35] W. Kodatzky, A. Schleede and F. Schroeder, *Physik. Z.*, **27**, 392 (1926); M. v. Ardenne, *Z. tech. Physik*, **16**, 61 (1935).

[36] O. Gaertner, *ibid.*, **16**, 9 (1935); M. Wiedemann, *ibid.*, **22**, 27 (1941).

[37] N. Riehl and P. M. Wolf, *Ann. Physik*, **11**, 108 (1931).

body color, as the fading of a dyestuff or darkening of a colorless or light-colored substance. It is due to a chemical transformation of the luminescent material.

For a time the hypothesis prevailed that in every case luminescence is only a secondary phenomenon accompanying some sort of chemical reaction.* This hypothesis was applied, for instance, by J. Perrin in order to explain the fluorescence of dyestuff solutions which were slowly bleached under the action of the exciting light.[38] The hypothesis seemed especially useful for the explanation of the so-called scintillations which are observed when α particles impinge on zinc sulfide screens and provide a method for the counting of α particles. Every individual α particle impinging on the fluorescent screen produces a sharply localized burst of light emission which was ascribed to the "breaking up" of some kind of "centers" in the material of the screen. The high efficiency of α-ray fluorescence, however, and the relatively slow rate of deterioration of the screens proves that it is not possible that every emission process is linked to the destruction of an emitting center.

A chemical transformation of luminescent molecules accompanying the excitation of fluorescence can be produced by three different processes.

A. In the most frequent cases of photoluminescence the absorption of the exciting light brings the molecule directly into the electronic state from which the emission takes place (compare Fig. 2). While in this state the molecule is highly reactive, and if a substance is present with which it can react, this reaction, *e.g.*, an oxidation, may ensue before the molecule returns spontaneously to the ground state with fluorescence emission. Thus the reacting molecules are "quenched" and have no part in the fluorescence.† In most cases the reaction products, *e.g.*, the oxidized dyestuffs are stable, and if they are not luminescent they are lost completely for further excitation processes. Eventually the solution fades and its fluorescing power disappears. If the reaction product is unstable, the process is reversed in the dark and the fluorescing power is restored. There is no

* In real chemiluminescence the light emission is frequently due to molecules which do not partake in the reaction. The energy set free by the reaction is transferred to non-reacting molecules. This statement is proved by the fact that the luminescence spectrum is characteristic of these and not of the reaction products.

† Nevertheless it is not mere coincidence that fluorescent compounds are in general very sensitive photochemically. They owe both properties to the fact that they are able to remain in an excited state a comparatively long time without converting the absorbed energy into heat. The same property enables them to transfer this energy to some other compound in a "collision of the second kind" and makes them good photochemical sensitizers. Here again it is not the fluorescence itself which plays a part in the energy transfer. As a matter of fact the best sensitizers are not the dyestuffs with the highest fluorescence yields.

[38] J. Perrin, *Ann. chim. phys.*, **10**, 133 (1918) and **11**, 5 (1919).

permanent fading, but only a "fatigue." The fading reaction can be inhibited if the reacting substance, most frequently oxygen, is removed.*

B. If photoluminescence is produced by light of shorter wave-length, the absorbing molecule is raised into an excited state of greater energy. It is possible that this energy is sufficient to break up the molecule by dissociation, and that from the excited state either return to the ground state with fluorescence or dissociation has a certain probability. Such molecular states are known as states of predissociation. In this case the eventual destruction of the fluorescence power does not depend upon the presence of any reacting foreign molecules. The fluorescent molecules, however, are again those which are not decomposed.†

Examples of these two types of fading processes are numerous amongst both organic compounds and inorganic phosphors. For example an aqueous solution of aesculin in contact with the atmosphere loses about 60 per cent of its fluorescing power when exposed in a glass tube to the radiation of a mercury arc for 1 hour. The active wave-lengths are longer than 3300 Å in this case. In an evacuated glass tube the fluorescence power remains constant during an irradiation period of thirty hours. In a quartz tube evacuated and sealed off, the intensity of the fluorescence decreases after two hours to 19 per cent of its initial value. This loss is due to the action of the mercury lines of wave-lengths below 3300 Å.[39] As a general rule it can be stated that organic and inorganic fluorescent materials are much less subject to fading if they are carefully protected from oxygen and in some cases from water vapor.

C. If luminescence is excited by x-rays, cathode rays or α-rays, the primary effect is, as already stated, a complete ejection of electrons from their normal location in the crystal lattice and thus a partial local destruction of this lattice.‡ However, these ionization processes are not the immediate source of light emission and the fluorescing "centers" excited by the secondary electrons are not destroyed but take part in many consecutive emission processes.

At high cathode ray densities (700×10^{-6} amp. per sq. cm.), screens of $CaWO_4$, Zn_2SiO_4, or ZnS are blackened in a relatively short time (half an hour) of continuous irradiation, apparently by the dislodging of free

* If the photochemical reaction is a polymerization of the fluorescing molecules as in the formation of dianthracene from anthracene, it cannot be inhibited by purification, though it may be reduced by decreasing the concentration.

† Absorption of light of still shorter wave-length leading exclusively to dissociation and not at all to fluorescence is of no interest in this connection.

‡ Only inorganic crystal phosphors are practically important for this kind of luminescence.

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[39] J. C. McLennan and F. M. Cale, *Proc. Roy. Soc. London*, **A102,** 256 (1922); N. C. Beese and J. W. Marden, *J. Optical Soc. Am.*, **32,** 317 (1942).

metal atoms from the lattice. Simultaneously the luminosity decreases, perhaps in consequence of the heat produced by the impinging electrons. Both fatigue effects are reversible. When the electron bombardment is interrupted the screen recovers its initial luminosity and color.[40] A permanent deterioration occurs only after several hundred or even thousand hours, depending upon the intensity of the irradiation.

Further properties of luminescent materials and phenomena connected with the production of luminescence such as photoconductivity, influence of electric and magnetic fields, polarization of the radiation, and the exact laws of growth and decay are very important for the development of a complete theory, but are of no special interest for practical applications and shall therefore not be taken into consideration here. Other phenomena like the quenching of fluorescence by certain substances or by infrared light will be dealt with in later chapters.

[40] W. Grotheer, *Z. Physik*, **112**, 541 (1939).

CHAPTER III

EXPERIMENTAL TECHNIQUE

1. Sources of Primary Radiation

a. Light Sources for Photoluminescence

The luminescence of different materials is excited by light of very different wave-lengths, and according to the spectral region wanted, different light sources must be employed.

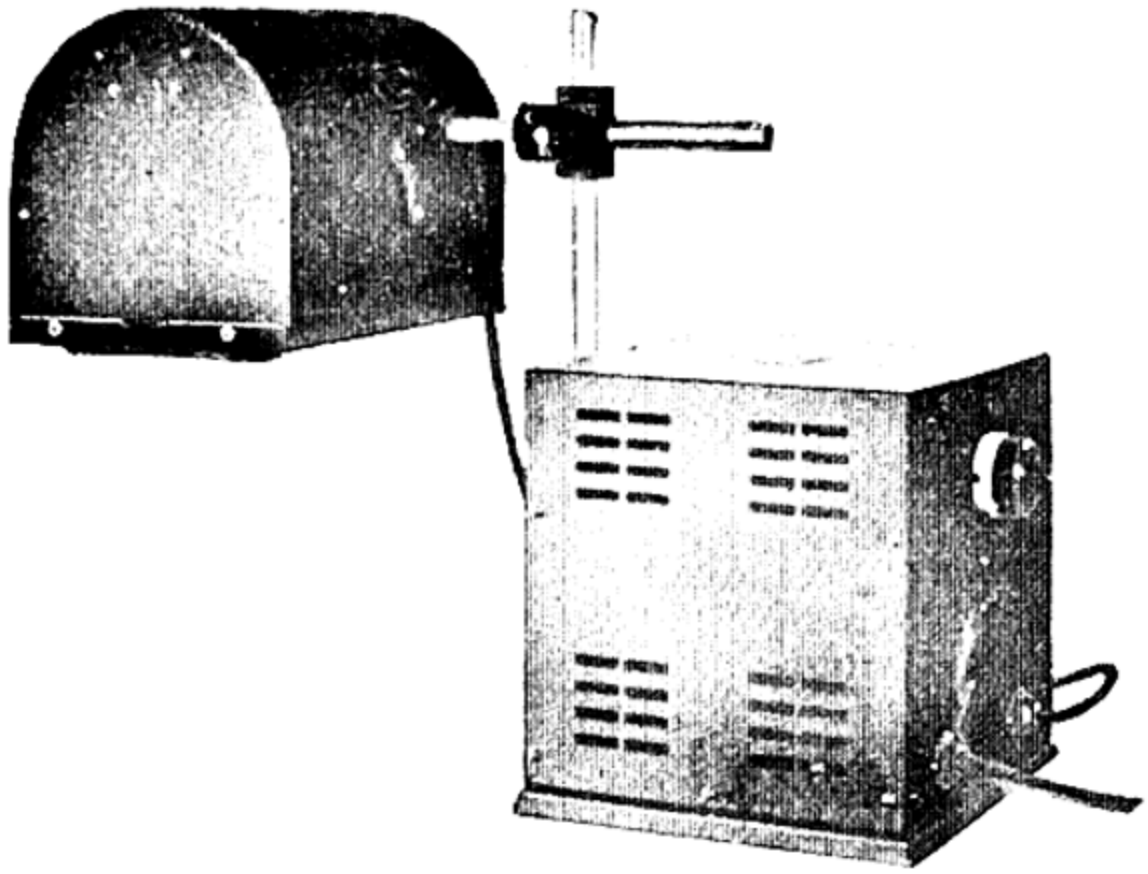
The most useful of all sources are quartz mercury arc lamps of which a great many models are now manufactured. The modern mercury lamps, filled with argon at a pressure of a few mm. Hg and containing only a small quantity of mercury, have several advantages over the older all mercury arc lamps of the Cooper-Hewitt type. The lamps need not be tilted or moved to strike the arc, they are switched on like any other electric lamp. They require a much shorter time to reach their full intensity. If the current is maintained constant their emission is constant over long periods of time within one per cent. The heat radiation is relatively small. Though they need a higher voltage than that provided by the normal house lighting circuits, this is not too serious a disadvantage since they are usually sold together with a small and easily transportable transformer. When switched off after a period of burning, they must cool down for a while before they can be struck anew. The same is true for the Cooper-Hewitt lamps.

For many purposes the small commercial H4 lamp of the General Electric Company, Westinghouse Company and other firms designed for illumination will be sufficient, but if the far ultraviolet part of the spectrum is desired the outer glass tube has to be discarded. For higher intensities the analytic quartz lamps made by the Hanovia Company and similar burners will prove themselves adequate (Fig. 16, a and b). The very highest energy from a small surface is provided by the watercooled high pressure mercury lamps. At the other end of the scale we find a small model, for outdoor use with a transformer operated by a 6-volt battery and vibrator.

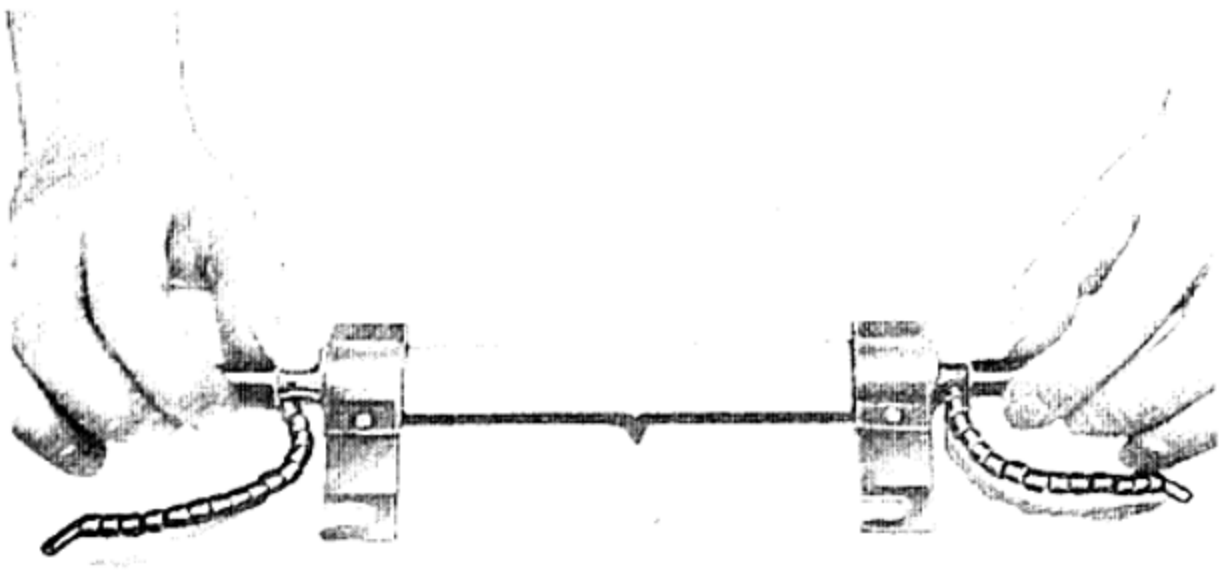
The spectrum of the mercury arc (Fig. 17) consists of a number of strong lines in the ultraviolet region, the strongest of which are at 2537, 2652/55, 3126/32 and 3650/62 Å. In the visible region there is a strong violet line at 4047 and a blue line at 4358 Å, followed by a rather large gap, and then a green-yellow line at 5461 and a yellow doublet at 5770/91 Å. The intensities of the lines in the ultraviolet beyond 2537 and in the red part of the spectrum are relatively weak.

It would not be of great use to insert a table giving the numerical values

of the relative intensities of the single mercury arc lines. Tables of this kind have been published by many authors[1] and they are probably quite correct, but only for the special case for which they were worked out. The data for different types of lamps, however, differ widely and even for the same burner the relation between the intensities of two or more lines



a



b

Fig. 16.—Analytic lamp (with kind permission of Hanovia Chemical and Mfg. Co.). a: Lamp complete. b: Quartz burner for alternating current.

may be completely reversed by changing the voltage and the current density under which the lamp is operated. Thus in the argon-filled low

[1] E. Ladenburg, *Verhandl. deut. phys. Ges.*, **9**, 504 (1907); W. Andersen and L. T. Bird, *Phys. Rev.*, **32**, 291 (1928); E. Beesley and H. N. Ridyard, *J. Phys. Chem.*, **32**, 1342 (1928); F. Roessler, *Ann. Physik*, **34**, 1 (1939); J. A. Leighton and G. S. Forbes, *J. Am. Chem. Soc.*, **51**, 3549 (1929).

pressure Hg lamps the relative intensity of the resonance line 2537 Å is highest at small current density;* in the high pressure lamps of the Cooper-Hewitt type the lines in the ultraviolet part of the spectrum, including the resonance line, become relatively much stronger with increasing voltage. On the other hand the line 2652 Å has only about 17% of the intensity of the resonance line when the Cooper-Hewitt lamp is operated at 3 amps., while it is appreciably stronger than the resonance line at 4.5 amps. In high pressure lamps at high temperatures the resonance line is completely reversed and appears in the emission spectrum as a dark line on a continuous bright band.

Fig. 17.—Spectra of different light sources on orthochromatic plate.

a: Hg quartz burner.
b: Same taken through Jena filter U.G. 5.
c: Same taken through Wood filter (Corning).
d: Carbon arc.
e: Same through Wood Filter (Corning).
f: Iron spark.
g: Same through Wood filter.

For most purposes connected with fluorescence work the list of the strongest Hg lines, as given above, will be sufficient. If for some special reason the relative intensities of two lines are needed, either the exact data for the lamp used under precisely defined electrical conditions must be known, or the intensities must be measured by means of a thermopile.†

For visible light and the near ultraviolet the most powerful source is still the positive crater of a carbon arc, especially if wave-lengths other than

* Special arc lamps "Sc 2537" with about 90 per cent of their total light output concentrated in the line 2537 are manufactured by the Hanovia Co. They are of great value for laboratory research work, but will probably be seldom used for technical applications. However, compare page 155.

† The "heterochromatic photometry" described on page 56 may also be useful in certain cases.

those of the comparatively few Hg lines are required. This source gives a spectrum that corresponds closely to continuous black body radiation of about 3000° C., which may be in some cases an advantage and in others a disadvantage.*

The rather rapid burning of the carbon electrodes constitutes a drawback which can, to some extent, be overcome by clockwork regulation or still better by an electromagnetic device. Even then, however, the intensity is never very constant and the exact position of the positive crater moves forward and backward. In this respect tungsten filament lamps, of the type used in cinematography, are by far more reliable, but though their total light output can be made very high, their brilliancy (intensity per square centimeter) is much smaller than that of a carbon arc. A rather weak but occasionally useful source of near ultraviolet radiation is provided by the small commercial argon glow lamps.

Almost continuous spectra of great intensity in the ultraviolet down to the limit of air transparency are emitted by low voltage arcs or high voltage

TABLE VI

REFLECTING POWER OF SILVER AND ALUMINUM

Wave-length of light		6000	5000	4000	3200	3000	2200 Å
Reflecting power (in %)	Ag	94	92	80	5	15	28
	Al	89	90	90	82	82	82

sparks between iron electrodes. The iron arc engenders much vapor and can be used only when good ventilation is available. This is not the case with the spark produced by a transformer with a capacitance and self-inductance in parallel. For the spectral region below 2000 Å, a spark between aluminum electrodes (strong lines at 1855, 1863, 1990, and 2095 Å) is even more effective.† The still shorter wave-lengths of the Schumann and Lyman region are used for the production of luminescence in some fluorescent lamps. This problem will be treated in a later chapter.

If the illumination is to be intensified by means of reflectors, aluminum is by far the best material. The reflecting power of silver is somewhat higher in the spectral region above 5000 Å, but at 4000 Å it drops below

* In spectrograms of the carbon arc there occur, superimposed on the continuous spectrum in the extreme violet and near U.V., the so-called cyanogen bands. These bands, which exhibit fine structure, originate not at the glowing anode, but in the arc itself. They must not be taken for a part of a fluorescence spectrum excited by the arc.

† Such sparks are not only very noisy but are also apt to perturb amplifiers used with a photoelectric photometer.

that of aluminum, and while the latter remains almost constant down to 2000 Å, the reflectivity of silver shows a low minimum of only 5% at 3200 Å (Fig. 18).[2]

For illumination of highest intensity the scheme reproduced in Fig. 19 has been worked out by R. W. Wood.[3] The fluorescent solution is contained in a cylindrical tube Fl and surrounded by a concentric tube W, the

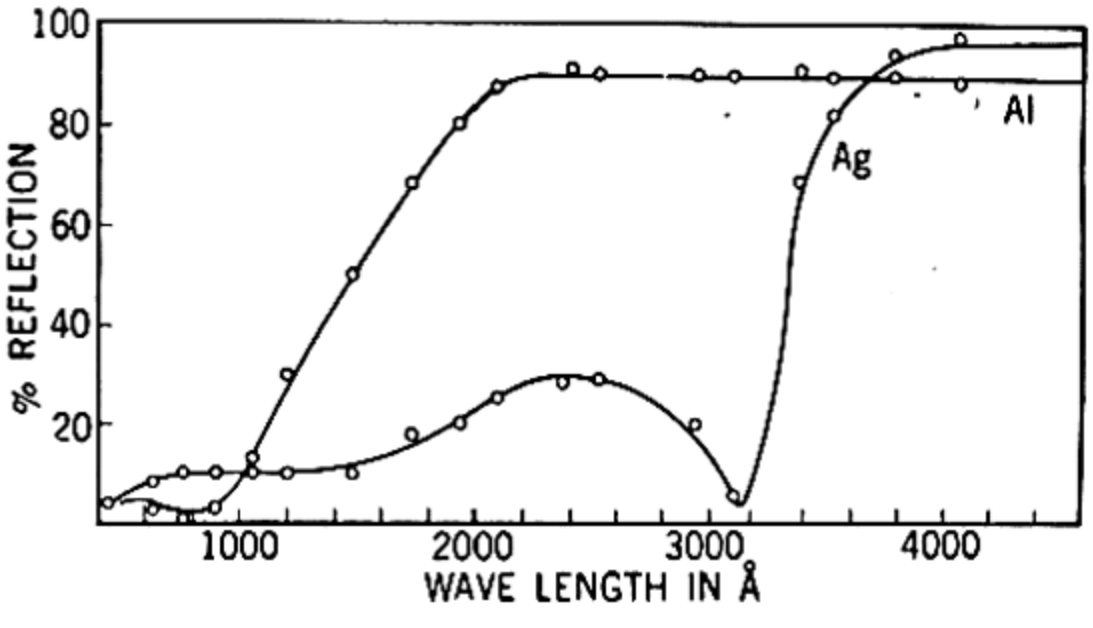


Fig. 18.—Reflectivity of silver and aluminum in the visible and ultraviolet parts of the spectrum (Sabine).

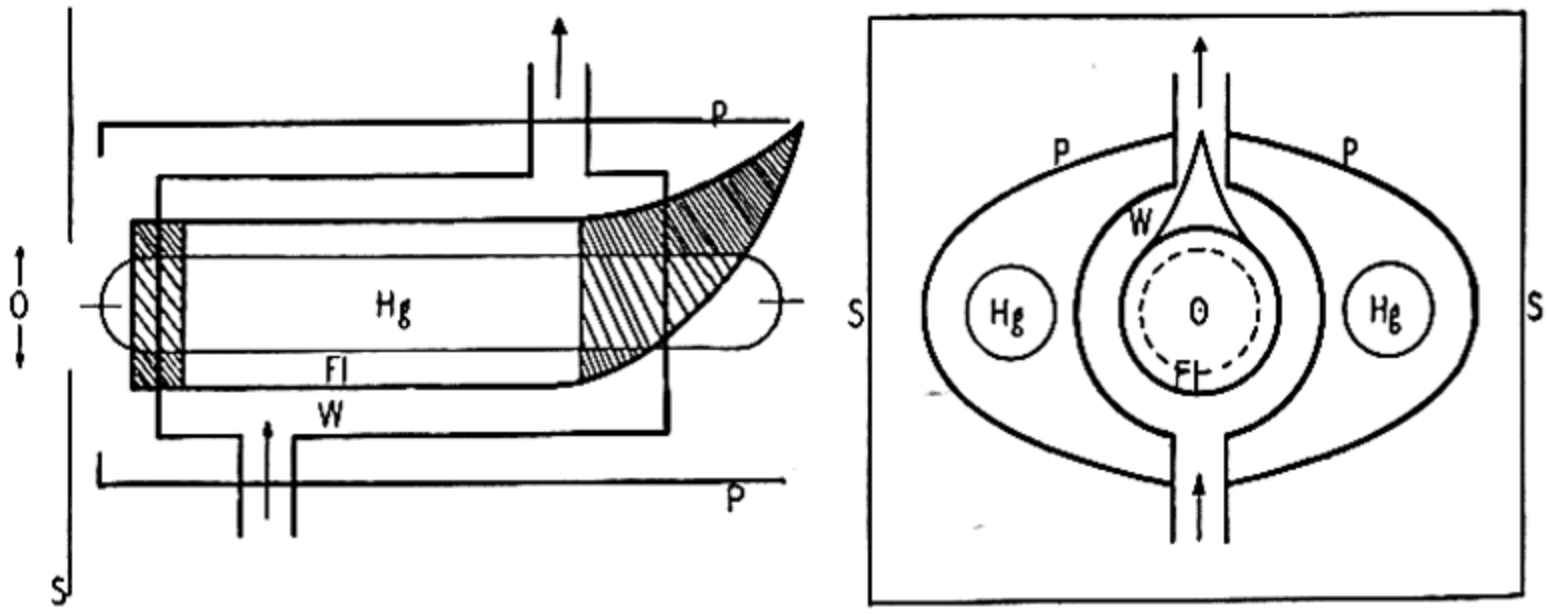


Fig. 19.—Wood's device for high intensity excitation of fluorescence.

purpose of which is to circulate cool water and also to act as a light filter. Alongside the tube mercury lamps of equal length are placed and the whole setup is enclosed in an elliptical cylindrical aluminum reflector. The fluorescent tube is observed "end on," the primary light being screened off by a diaphragm.

b. Filters and Monochromators

For every observation of photofluorescence it is desirable that the exciting light, diffused or reflected by the luminescent substance, is not super-

[2] G. R. Sabine, *Phys. Rev.*, **55**, 1063 (1939).
[3] R. W. Wood, *Phil. Mag.*, **6**, 729 (1928).

TABLE VII

LIGHT FILTERS FOR THE ISOLATION OF Hg LINES

Wave-Lengths			
2480 Å 2537 Å	200 g. $NiSO_4 \cdot 6\text{-}7H_2O$ + 50 g. $CoSo_4$ in 1 liter water, 10 cm. thick	Cl_2 – gas 1 atm. 3 cm. thick	0.108 g. I_2 + 0.15 g. KI in 1 liter water, 1 cm. thick*
2655 Å			$HgCl_2$ in water, 45 g. per liter,** 1 cm. thick or KI in water, 1.7 g. per liter,* 1 cm. thick
2755 Å 2802 Å			
2895 Å 2925 Å 2970 Å 3030 Å		Oxalic acid in water, 20 g. per liter, 1 cm. thick,* or $CuSO_4 \cdot 5H_2O$ in water, 15 g. per liter, 1 cm. thick	
3126 Å 3132 Å		Potassium hydrogen phthalate in water, 5 g. per liter, 1 cm. thick	
3341 Å		Uric acid saturated in water, 1 cm. thick	
3650 Å	4.4 g. $CuSO_4 \cdot 5H_2O$ + 150 gr. NH_4OH (density 0.88) in 1 liter water, 10 cm. thick	Wood filter	
4047 Å		I_2 in CCl_4, 7.5 g. per liter, 1 cm. thick + quinine hydrochloride in water, 10 g. per liter, 2 cm. thick*	
4358 Å		75 g. $NaNO_2$ in 100 cc. water, 2 cm. thick**	
5461 Å	13 g. $CuSO_4 \cdot 5H_2O$ + 0.44 g. $K_2Cr_2O_7$ + 50 cc. H_2SO_4 in 1 liter water, 10 cm. thick	Corning glass 512, 5 mm. thick (didymium glass)	
5770 Å 5791 Å		Corning glass 344, 3.5 mm. thick (orange glass)	

* Renew frequently.
** Renew occasionally.

imposed on the luminescent radiation.* The simplest way of avoiding this complication is provided by Stokes' crossed filter method.[4] In this scheme

* If this is not avoided, erroneous estimates of the fluorescence color may result. As an example we quote the table of fluorescent rhodamine dyestuffs in Feigl's excellent book on analysis by spot tests, page 301, where the color of fluorescence is stated to be different when excited by daylight or by U.V. radiation. The apparent difference is due only to the reflection of the daylight.

[4] G. Stokes, *Phil. Trans.*, **143 II**, 463 (1852).

the light source is enclosed in a box with a single opening, and a colored glass, which serves as window, transmits only the spectral region wanted for excitation. The fluorescent light is viewed through a second light filter which transmits the fluorescence and is complementary to the first filter. Colored glasses of almost every hue are manufactured by the Corning Glass Company and other firms. They are, if available, to be preferred to liquid solutions or gelatin-coated plates stained with organic dyestuffs. These, in general, are bleached by long exposures to strong ultraviolet radiation.

In most cases actually described as "fluorescence analysis," and for many other applications of photoluminescence, the fluorescence is excited by light in the near U.V. region. A black glass, made almost opaque to visible light by its content of nickel oxide and known as a "Wood filter," transmits a great deal of ultraviolet light between 4000 and 3200 Å, the maximum

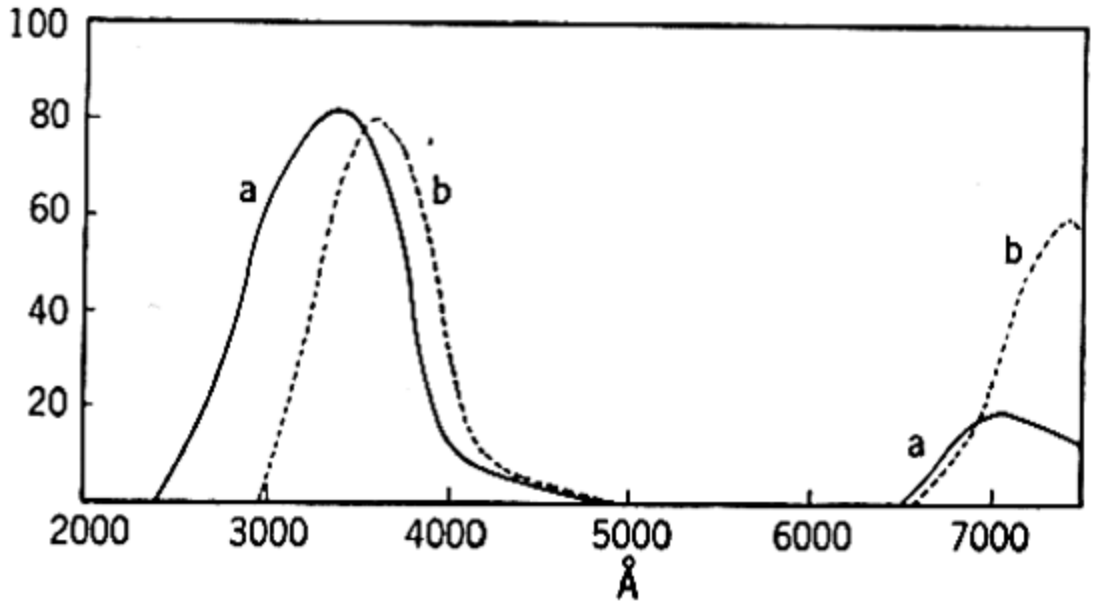


Fig. 20.—Absorption spectrum of two Corning ultraviolet-transmitting filter glasses.

a: Red purple Coren No. 986. b: Red purple ultra No. 597.

transmission corresponding to wave-lengths near 3600 Å (Fig. 20, compare also Fig. 17). With such a glass as an initial filter the second filter can be omitted, since the human eye is only slightly sensitive to U.V.*

Mercury lamps of the different types mentioned above, equipped with Wood filters, are on the market under the names of analytical lamps, purple-X lamps, etc. So-called black bulb lamps, which are hot filament lamps enclosed in a bulb of heat-resisting black glass, are also available.

Many qualitative fluorescence experiments can be executed by merely exposing the luminescent material to the "black light" radiation of such a lamp in a dark room.

If higher intensity of the exciting light or a better definition of the primary beam is desired, an image of the source must be projected on the

* Nevertheless the eye should not be exposed to the U.V. radiation, for this produces fluorescence in the eye lens and thereby a strong sensation of glare.

sample by means of lenses. Ordinary glass does not absorb the near U.V. transmitted by a Wood filter, and hence glass vessels and glass lenses may be used in combination with such filters. It must not be forgotten, however, that simple glass lenses have a strong chromatic aberration in the region of shorter wave-lengths, so that the focusing must not be effected with visible radiation. The nickel oxide filters, opaque for nearly the whole visible spectrum, transmit red light beyond 6500 Å. These longer wave-lengths are not completely missing from the Hg-arc radiation and are very strong in the radiation from a carbon arc or a hot filament lamp. In order to cut off this light, which might interfere with the visual observation of weak fluorescence, a second screen—either an aqueous solution of $CuSO_4$ or a glass of similar absorbing power—is frequently placed in the path of the exciting beam. Such filters, though perfectly transparent for the greater part of the visible spectrum, start to absorb again below 4000 Å, and if they are sufficiently dense to eliminate all red light, they cut down the U.V. radiation at 3600 Å and, therefore, the fluorescence intensity by more than one-half. If, therefore, the fluorescence itself is not red, it is advisable to place this screen between the fluorescent material and the observer's eye. On the other hand a cell of at least one inch thickness filled with water, or some special glass filter absorbing infrared radiation, must always be placed in the path of the primary light beam, if a carbon arc or a filament lamp is used as source. This is done in order to protect the luminescent material and other filter glasses (especially the black glass) against overheating.*

At wave-lengths below 3200 Å, practically all types of glass absorb strongly, and quartz must, therefore, be used for lenses and containers. In some cases it is sufficient to provide the latter with quartz windows.

Fused quartz specimens from different sources vary greatly in their transparency to ultraviolet light. This is probably due to impurities contained either in the raw material or dissolved in it during the process of fusing. Thus, some specimens begin to fluoresce when exposed to the radiation of the mercury line 2537 Å, while others do so only under illumination by an iron arc or even an aluminum spark. The appearance of fluorescence is a reliable indication that the quartz under observation absorbs light of the respective wave-length.†

* Some "black" glasses, like Corning red purple, 587, are qualified as "heat resisting." But apart from the fact that these glasses have a smaller transmission power for ultraviolet radiation, even they are liable to crack if the concentrated light of a carbon arc is focused upon them without the interposition of a screen absorbing the infrared radiation.

† Quartz windows, fused onto a hydrogen or helium discharge tube, always exhibit a strong fluorescence and a long lasting afterglow which are excited by the "Schumann and Lyman radiation" emitted by the discharge.

For wave-lengths shorter than 2100 Å fused quartz is no longer serviceable, while good crystalline quartz is transparent to about 1850 Å, the very limit at which atmospheric oxygen begins to absorb all radiation.* The observation of the weak fluorescence of a substance contained in a tube can be rendered difficult by the fluorescence of the tube material. If the latter can not be screened off by the use of adequate filters, the observer's eye must be brought into such a position that it does not intercept any light coming from an illuminated part of the walls of the container. This may be achieved either by "backward" observation from above, if a liquid solution can be placed in an uncovered container (Fig. 32), or by "sidewise" observation, the side walls of the tube being well shielded against the primary beam and the entrance window being hidden from the observer's eye (Fig. 31).

Of course, it is always advisable to choose a container with as little fluorescence of its own as possible. Certain types of glass are in this respect

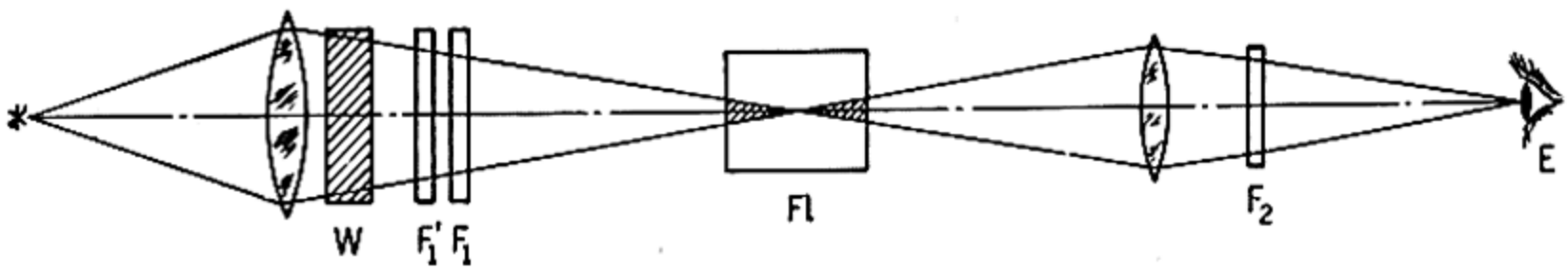


Fig. 21.—Setup for "forward observation" of fluorescence.
W: water cell. F_1', F_1, F_2: filter.
Fl: fluorescent substance. E: eye of observer.

much better than others.† The container need not be transparent for backward observation and in this case porcelain dishes are very useful. Since they are white, they show that part of an observed radiation which may be due to reflected visible light transmitted by the "black" screen.‡ Solid powders are best supported by a plate of metal like copper or brass, for these are never luminescent. If a fluorescent solution is to be investigated when adsorbed on filter paper, it is again important that the paper should

* For the Schumann region, calcium fluoride and lithium fluoride are the only transparent materials available, but this will be of little interest in technical applications.

† Under black light illumination some varieties of soft glass, pyrex, thermometer glass, and Jena suprax show scarcely any fluorescence, while other types of soft glass and pyrex emit a strong yellowish, and Jena durax a strong orange-colored, fluorescence.

‡ The well-known dishes of the Berlin porcelain factory do not fluoresce, even when illuminated by the light from an iron spark, with the exception of spots where the glaze is destroyed. Some porcelain of other manufacture shows a whitish blue fluorescence when irradiated with light of wave-lengths shorter than 3000 Å, but remains dark in black light.

not fluoresce itself under the action of the exciting black light.* If for some special reason fluorescence is to be observed "forward" (Fig. 21), the two filters F_1 and F_2 must be more nearly complementary than in any other case, so that no primary light can reach the observer's eye. If at the same time F_1 (colored glass or dye solution) is fluorescent under the action of the total primary radiation, F_2 must be chosen so that it is opaque to the fluorescence of F_1. As a general rule it is always useful to place a primary filter which absorbs all light of wave-length shorter than the radiation needed for excitation next to the light source, and then behind it the screens used for cutting off the longer wave-lengths. This will often avoid the undesirable fluorescence of the latter screens.† Besides, many luminescent substances are decomposed by the action of short wave-length ultraviolet light and their luminescence properties thereby altered or lost, as was pointed out in the last paragraph of the second chapter.

Occasionally photoluminescence is to be investigated when it is excited by light confined to several narrow spectral regions. Under these conditions quartz monochromators give the best results. A monochromator is a spectrometer with a second slit E_2 in the plane upon which the spectrum is focused; hence the image of E_2 may be projected on the fluorescing sample *Fl* by means of quartz lens L_3.‡ For wave-lengths below 3500 Å, the chromatic aberration of quartz must not be neglected, so that for every change in illuminating wave-length the two inner lenses L_1 and L_2 of the monochromator and the outside lens L_3 have to be readjusted. Using a slit-width of 0.5 mm., all spectral lines of the mercury arc (for example 2895, 2802, and 2755 Å) are isolated by a commercial Bausch and Lomb quartz monochromator with reasonable intensity. The brilliancy of spectral lines can usually be increased a good deal by the use of a cylindrical lens L_4,** which, leaving the length of the spectrum unchanged, shortens the heights of the individual lines.

If no monochromator is available, a convenient combination of filters may be used instead, especially if the spectrum of the primary light is not

* This refers to so-called capillary tests (see page 102). Non-fluorescent papers of European manufacture have been listed by Feigl in his book on spot reactions, and perhaps equivalent filter papers could be found in this country.

† The heat-absorbing water cell mentioned above should always be placed next to the source.

‡ In the setup of Fig. 36 a "double monochromator" is used for better isolating the spectral lines. In this case the exit slit E_2'' of the first half of the instrument serves as entrance slit for the second half, while E_2 is the final exit slit. If the line focused on E_2' contains 1% of stray light, the "impurity" is reduced to 0.01% by this instrument.

** A good transparent quartz tube filled with water may serve as a cylindrical lens.

continuous but consists of well-separated lines.* For the isolation of all of the stronger Hg lines Bowen has compiled a list of filters reproduced in Table VII.[5] (See p. 41.) In his arrangement the first liquid solution is contained in a spherical glass or quartz flask which serves at the same time as a condensing lens (see Figs. 31 and 32).

Other filter combinations may be found in Wood's *Physical Optics* and elsewhere. Corning filter 986 and Jena UG5 which are not quite as opaque to visible light as the other "black glasses," transmit the Hg line 2537 Å fairly well. As a monochromatic filter for the Hg line 3130 Å, Wood recommends a silver film deposited on a quartz plate or a quartz lens (the minimum of reflecting power of the silver coincides very nearly with this line).† If all ultraviolet light is to be screened off, Corning Noviol glass or an aesculin solution are useful.

c. Cathode Rays, X-Rays and α-Rays

Only solid substances are to be considered for the excitation of luminescence by cathode rays, and among these, the most important by far are the inorganic "phosphors." It is true that many organic compounds are strongly luminescent under electron bombardment, but they simultaneously undergo chemical transformations of an unknown nature by which their luminescent properties are completely altered. To a certain degree the same may occur with mineral phosphors. Their stability, however, is of a higher order, especially if no gas is present in the cathode ray tube, as is always the case in modern apparatus. These are highly evacuated and provided with an "electron gun," a hot filament electron source with an electrostatic device to concentrate the cathode rays into a narrow and well-defined beam. In such tubes the current density (amps. per sq. cm.) and the voltage can be altered independently.‡ With normal accelerating voltages (below 100,000 volts) the luminescent material has to be placed inside the tube. The inorganic phosphors are in almost every case bad conductors, and usually they are placed upon a transparent isolating support—*e.g.*, a glass or mica plate, which is surrounded by the anode of the tube (Fig. 22). Because of the impinging electrons the fluorescent screen would at once be charged up to a negative potential, were it not for the emission of secondary electrons by the screen material. As long as the number of these electrons is larger than the number of impinging electrons,

* The more "monochromatic" such a filter combination, the more it reduces, in general, the intensity of the light it is meant to transmit.

† It is easier to prepare a good silver film by sublimation in a vacuum (as is also the case for aluminizing a surface) than by the older method of precipitation from a silver salt solution.

‡ This is not the case in the old gas-filled cathode ray tubes.

[5] E. J. Bowen, *J. Chem. Soc.*, 1935, p. 76.

the positive potential of the screen does not fall below the positive potential of the anode. But with increasing energy of the primary electrons the

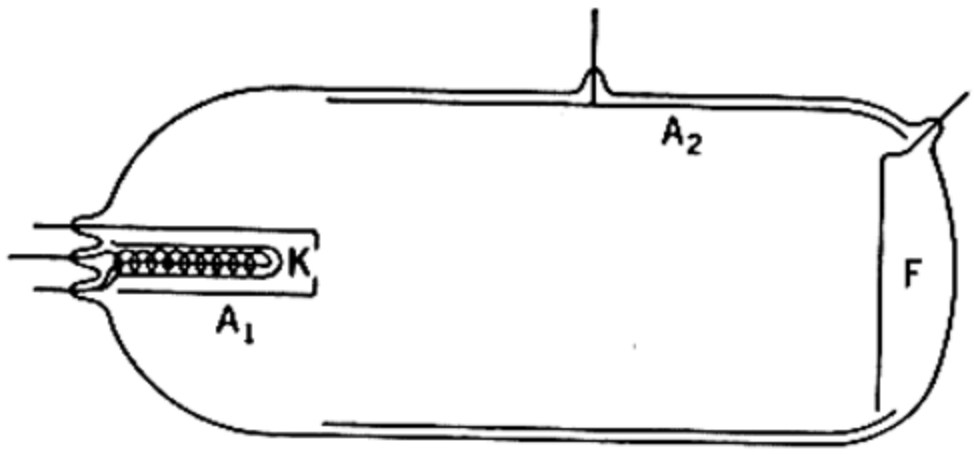
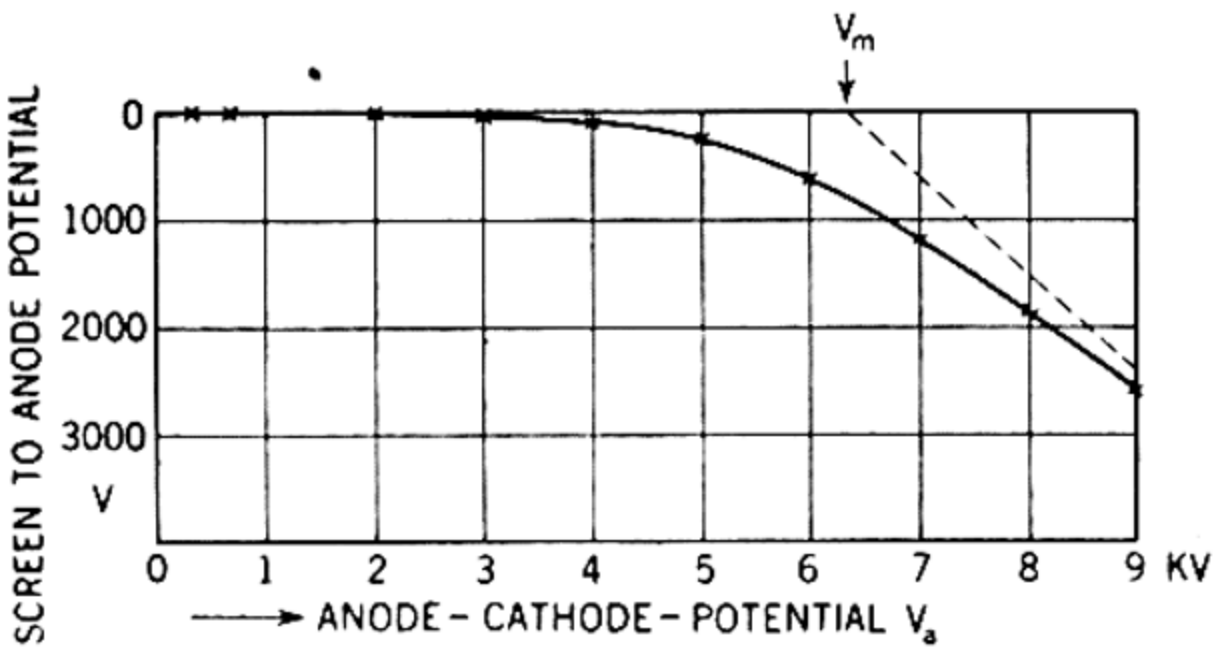
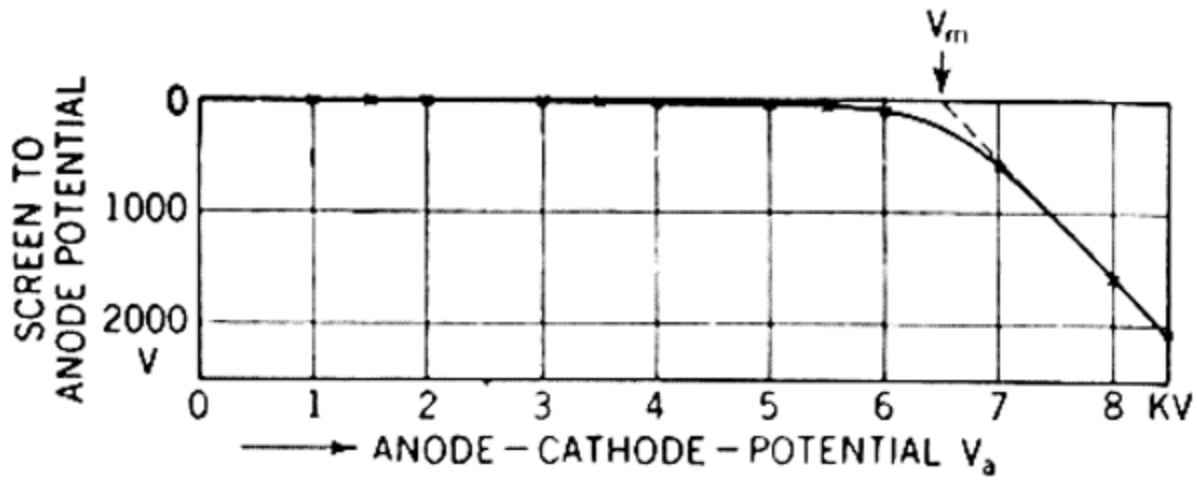


Fig. 22.—Tube for fluorescence excitation by cathode rays.
K: Indirectly heated cathode.
A_1: First anode. A_2: Second anode.
F: Fluorescent screen.



a



b

Fig. 23.—Screen potential as function of anode potential in cathode fluorescence tube (Nottingham).
a: Low current density. Ortho zinc silicate i = 0.12 ma./cm.²
b: High current density. i = 10 ma./cm.²

relative number of secondary electrons decreases, and when the ratio of the primary to the secondary electrons becomes equal to one, the maximum potential difference V_m between cathode and screen is reached. A further

increase of accelerating anode potential V_a does not alter the screen potential any further (Fig. 23).[6] The absolute value of V_m depends on the electron emissivity and on the electrical resistance of the screen material. In some cases V_m is as low as 5000 volts, in others it is far above 10000 volts.*

If for special investigations (analysis, yield measurement, etc.) the fluorescent substance has to be changed frequently, it is well to have the tube fitted with a wide ground stopper through which the exchange may be made. The tube must be permanently connected to a vacuum pump.† For most technical applications, however, as in oscillographs, electron microscopes, etc., sealed-off commercial tubes are always used. The same is true for any kind of x-ray tubes used for fluorescence excitation.

For α-ray excitation only two natural radioactive substances are actually to be taken into account: radium itself in equilibrium with its α-ray emitting products down to polonium; and mesothorium, which is a β-ray source but which produces radiothorium, an α-ray emitter.

2. Photometry

Though the designations "fluorometer" or "fluorimeter" are to be found in some scientific papers and in many advertisements, there exist no instruments which have been designed especially for the measurement of the intensity of fluorescence or phosphorescence. The methods used for this purpose are the same as for any other kind of photometry. They are visual photometry, intensity measurements by means of photoelectric cells, and photography, only the last two being available for ultraviolet light.‡

* F. Krantz proposes to overcome this limiting voltage by a simultaneous bombardment of the screen with slow electrons from a second cathode; by these a sufficient number of secondary electrons would be released and so the building up of a negative charge on the screen would be avoided.[7] By mixing the phosphorescent powder with the oxide of an alkaline earth the electron emissivity of the screen can be increased and the limiting potential V_m be brought to a higher value. Still another solution of the problem has been proposed by Guervain. He uses a screen made of a thin aluminum foil backed by the fluorescent material. The foil is directly connected with the anode and, therefore, always has the full anode potential. About 95% of the electrons accelerated by 50 kv pass through the metal foil and are thus able to excite the fluorescent material which is viewed through the glass of the tube.[8]

† If the tube must be baked out for every experiment in order to have it thoroughly outgassed, no ground joint may be used. The tube must be cracked and resealed for every new load.

‡ Chemical methods other than photography for the measurement of ultraviolet light intensities are no longer to be taken into account, at least as far as fluorescence work is concerned, though they are still discussed in detail by some authors. Though

[6] W. B. Nottingham, *J. Applied Phys.*, **8**, 762 (1937).

[7] F. Krantz, *Z. Physik*, **114**, 459 (1939).

[8] A. de Guervain, *Hochfrequenztechn. u. Elektroakustik*, **54**, 151 (1939).

Precision exceeding a few per cent is not easily obtained by any of these methods, but will seldom be needed for technical applications.

All photometry is based on the comparison of the light intensity that is to be measured with the intensity of a standard source. The comparison can be carried out either by two successive or two simultaneous measurements. If the primary lamp exciting the luminescence has a sufficiently constant energy, either method may be used. If this is not the case, as with a spark, a carbon arc, or a Cooper-Hewitt mercury lamp, the two measurements must be made simultaneously, the "standard" being illuminated by the same source which excites the fluorescence. For a quantitative comparison

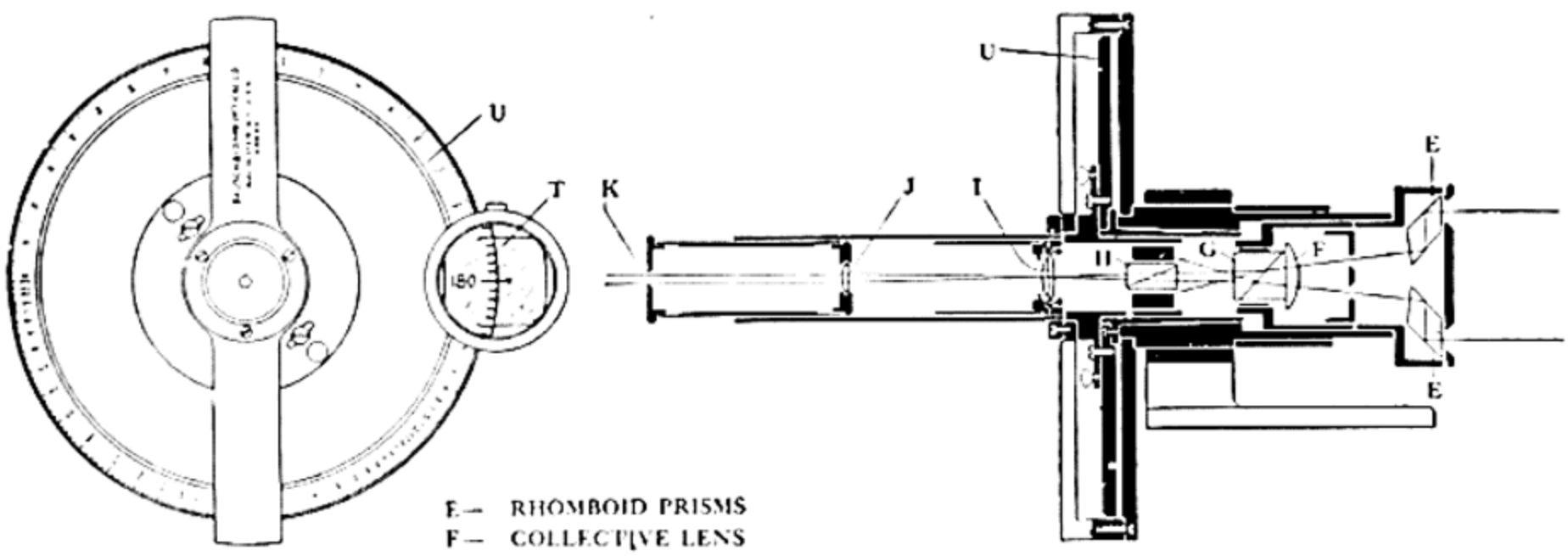


Fig. 24.—Koenig-Martens type polarization photometer (by courtesy of Messrs. Bausch and Lomb).

the intensity of the standard source, which may be supposed to be the brighter, is weakened by some device in a measurable way until the two intensities are equal. Among such devices are two polarizing prisms (Fig. 24) or polaroids* which can be rotated with respect to each other,†

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not accurate to within more than about 10 per cent, so-called photochemical actinometers are still used to good advantage for the determination of the quantum yield of photochemical reactions. As a matter of fact, the immediate purpose in this case is not really to measure light intensities, but to compare quantitatively the results of two photochemical reactions produced by the same irradiation, the quantum yield of one of the two reactions being known.

* The older polaroids could only be used for the central part of the visible spectrum, but the latest improvements make them serviceable for all visible light down to 4200 Å.

† Photometers of this type (Koenig-Martens photometer) should not be used without special corrections if the light is partially polarized before entering the first polarizing prism.

calibrated neutral wedges,* calibrated diaphragms of variable aperture (Fig. 25),† and rotating sectors with variable aperture.‡ The classical method of altering the intensity of one of the light sources by varying its distance from the receiving surface is also still used occasionally for the photometry of luminescent substances. However, several possible sources

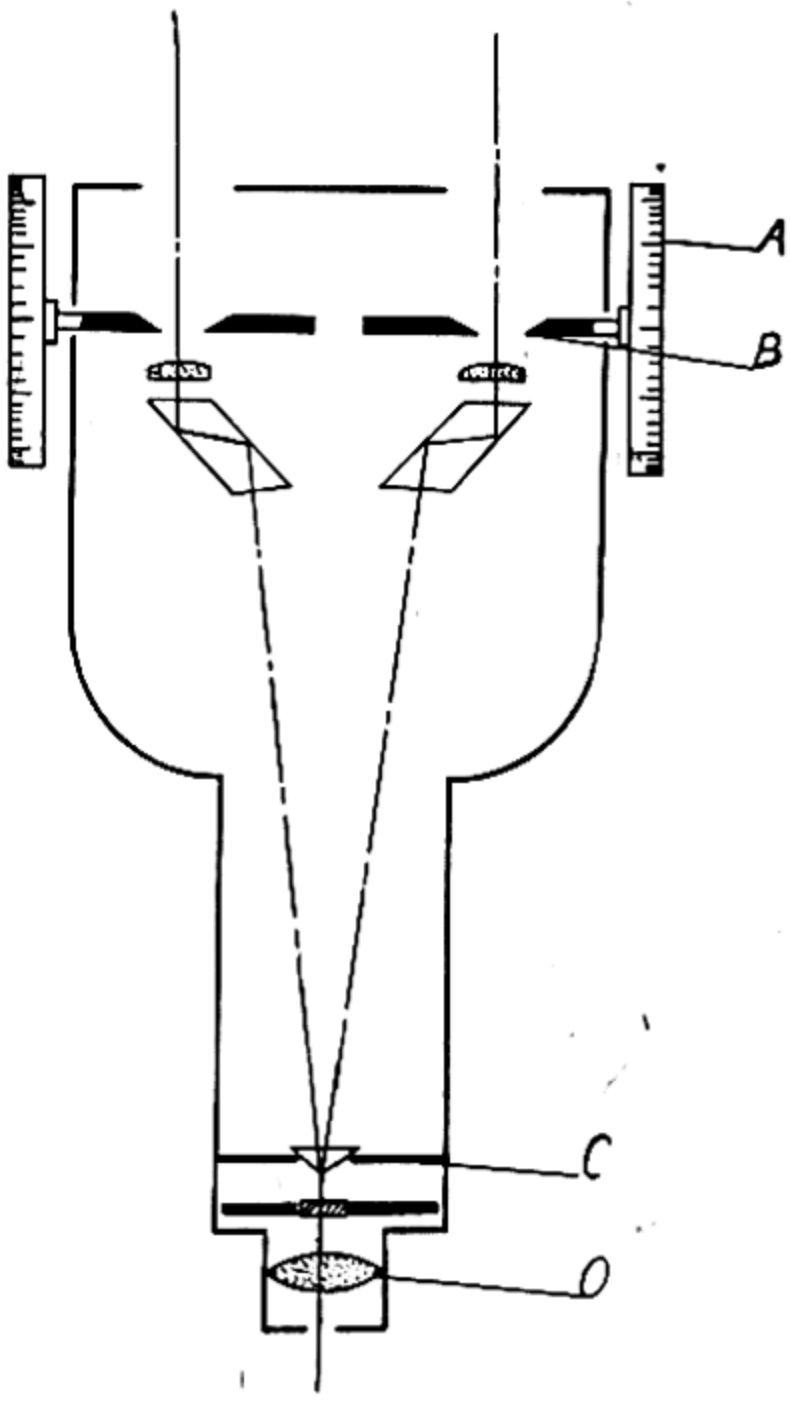

Fig. 25.—Pulfrich photometer with variable aperture ("Stufo").
A: Drum with scale.
B: Diaphragm with variable aperture.
C: Biprism.
O: Ocular lens.

of error must be taken into account, if accurate results are to be obtained with this apparently simple method.[9]

* This method has the disadvantage that if the wedge is fairly steep, a narrow slit must be used for good definition.

† Some of the best modern photometers are based on this method, but it is of the greatest importance that the position of the diaphragms remains permanently unchanged after calibration.

‡ The method of varying the depth of the scattering liquid, used frequently in nephelometry is not to be recommended for fluorophotometry because a part of the fluorescent light may be reabsorbed in the solution and this factor depends on the distance which the light has to travel inside of the solution. Still more objectionable for such measurements are "colorimeters" in which the length of the irradiated solution is variable, for with increasing length additional volumes of the solution contribute ever smaller amounts to the total fluorescence output.

[9] A. H. Taylor, *J. Optical Soc. Am.*, **32**, 506 (1936).

If the relative fluorescence intensity of a substance under different conditions (variable temperature or concentration of a solution, presence of quenchers, etc.) is to be investigated, it is best to compare these intensities J_1, J_2, etc., with a constant standard J_0 so that: $J_1 = \alpha_1 \cdot J_0$, $J_2 = \alpha_2 \cdot J_0$; hence by elimination of J_0:

$$J_1 : J_2 \text{ - - - } = \alpha_1 : \alpha_2 \text{ - - -}$$

It is absolutely necessary that the vessel containing the fluorescent substance should always be replaced at exactly the same position in front of the photometer. The standard is a fluorescent substance of the same nature as the one to be investigated, kept under strictly constant conditions and excited by the same primary source.

In visual photometry the two measurements mentioned above are always made simultaneously, since the human eye is only able to compare the intensity of two light sources if they illuminate two contiguous areas at the same time. A visual photometer can be set up with rather simple means in the laboratory,[10] but good manufactured instruments give, in general, more reliable results. For visible light and not too small intensities the results are probably at least as good as those obtained by any other method.

Two different kinds of photoelectric cells are available for photometry; barrier layer cells (photronic cells) and surface emission cells, these being either of the vacuum or of the gas-filled type. Barrier layer cells and gas-filled cells have higher sensitivity, but vacuum cells give more reliable results for exact quantitative research.

Many commercial light-meters and also some so-called fluorimeters are equipped with barrier layer cells. These have the advantage of being very compact and easily transportable, and function without an external electromotive force. Since amplifiers cannot be used with these cells, the currents must be measured with galvanometers of high sensitivity (10^{-9} -10^{-11} amp./mm.). The photoelectric currents are proportional to the light input only within rather narrow limits, but with the small intensities usually forthcoming in fluorescence research work this need not be taken into account. Most photronic cells are only serviceable for visible light, with a maximum of sensitivity between 6000 and 5000 Å: even in the violet region their response is sometimes exceedingly small (Fig. 26).

Emission cells with various cathode materials cover the whole spectral range from red to far U.V.* Most commercial photoelectric tubes are made

* Cs_2O-Ag_2O cathodes are most sensitive for the longer wave-lengths, but because of their high thermionic emission their dark current is relatively strong even at room temperatures, so that their use is not advantageous for photometry of weak intensities. K_2O-Ag_2O cells are most satisfactory for this spectral region, Cd or Na cathodes for wave-lengths around 3000 Å, and platinum or palladium cathodes below 2600 Å. The cells R.C.A. #929 with Cs on Sb are excellent for the whole spectral range from 6500 to the limit of glass transmission at 3300 Å.

[10] R. W. Wood, *Phil. Mag.*, **21**, 311 (1911).

of lime glass, and therefore their spectral sensitivity range is limited on the short-wave end by the light absorbing power of the glass. For instance, the steep slope below 3500 Å of curve *a* in Fig. 27 is due exclusively to the glass absorption, while the sensitivity of the photocathode itself would still increase with decreasing wave-lengths. For fluorophotometry this limitation will hardly be prejudicial in general. For intensity measurements in the region of shorter wave-lengths the photoelectric cells must be made of fused quartz or at least fitted with a quartz window* (Fig. 27,

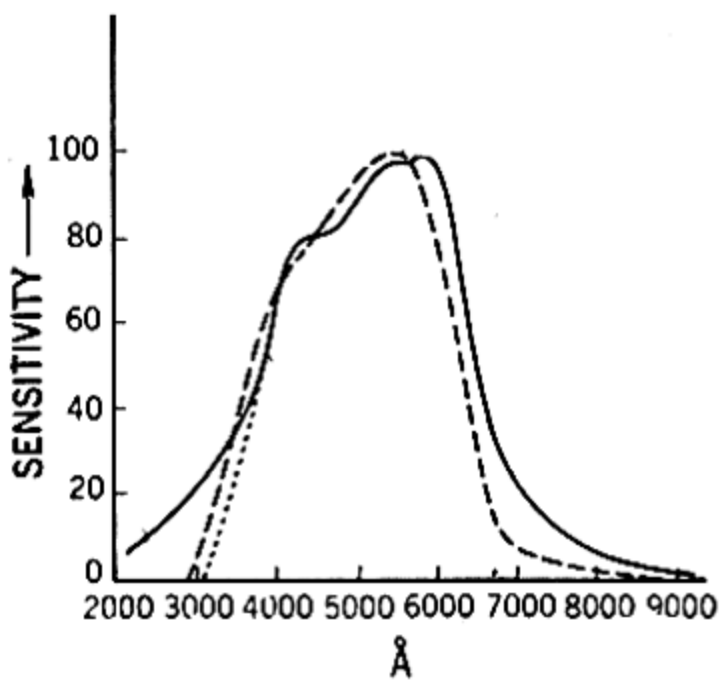

Fig. 26.—Spectral sensitivity of barrier layer cells.

——— Visitron F 3 photronic cell with quartz window (G. M. Lab. Inc., Chicago).
..... Same with glass window.
– – – – General Electric blocking layer cell protected by coating against atmospheric conditions and glass window.

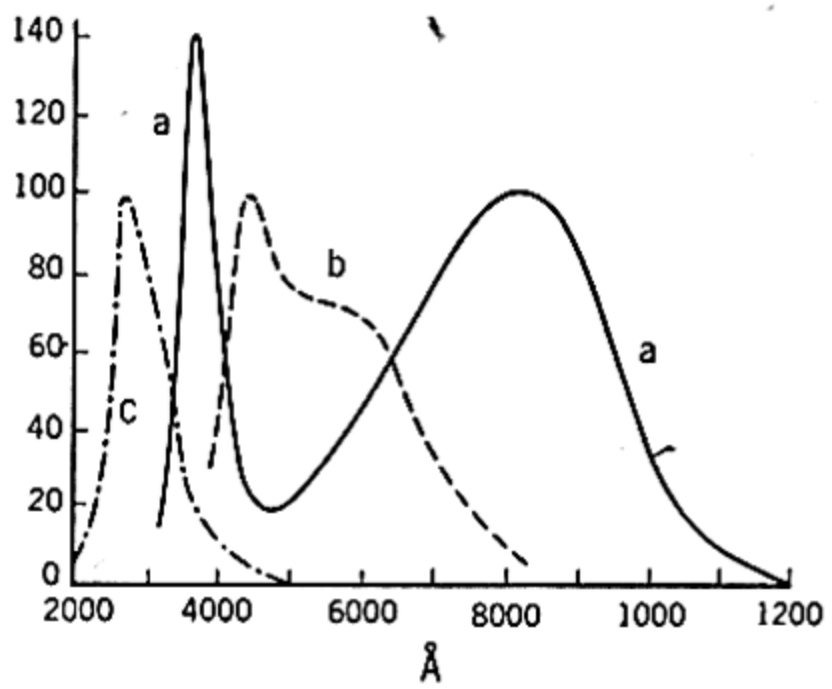

Fig. 27.—Spectral sensitivity of photoelectric cells.

a: R.C.A. S 2 photosurface in lime glass bulb.
b: R.C.A. S 3 photosurface in lime glass bulb.
c: General Electric Phototube F 405, sodium cathode in quartz tube.

Curve *c*). Gas-filled cells of many types are on the market, since they are in general use in the motion picture industry.

The photoelectric currents of vacuum cells are, in general, saturated at an anode potential of about 20 volts.† In gas-filled cells the molecules of the gas are ionized by collisions with electrons and thus the primary photoelectric current is amplified. For achieving this purpose the cells require potentials of from 100 to 200 volts to attain their maximum sensitivity. This sensitivity is very much influenced by small changes in the accelerating

* Windows of very thinly blown pyrex glass also transmit light of wave-length somewhat below 2530 Å.

† The exact value depends upon the construction of the cell.

potential, and besides there is a certain danger of a glow discharge which may spoil the cell.

The currents from emission cells can be easily amplified, the cathode being connected to the grid of an amplifying tube and shunted to its cathode through a high resistance (Fig. 28),* or they may be measured with an electrometer connected directly to the photocathode and shunted through a high resistance ($10^9-10^{11}\Omega$) to the ground (Fig. 29). If photocurrents of very different magnitude are to be compared, a null method in which the currents are compensated by means of a potentiometer allows the use of a highly sensitive galvanometer or electrometer (Fig. 29).

Since the photoelectric currents are proportional to the intensity of illumination, no standard comparison source is needed if the primary light

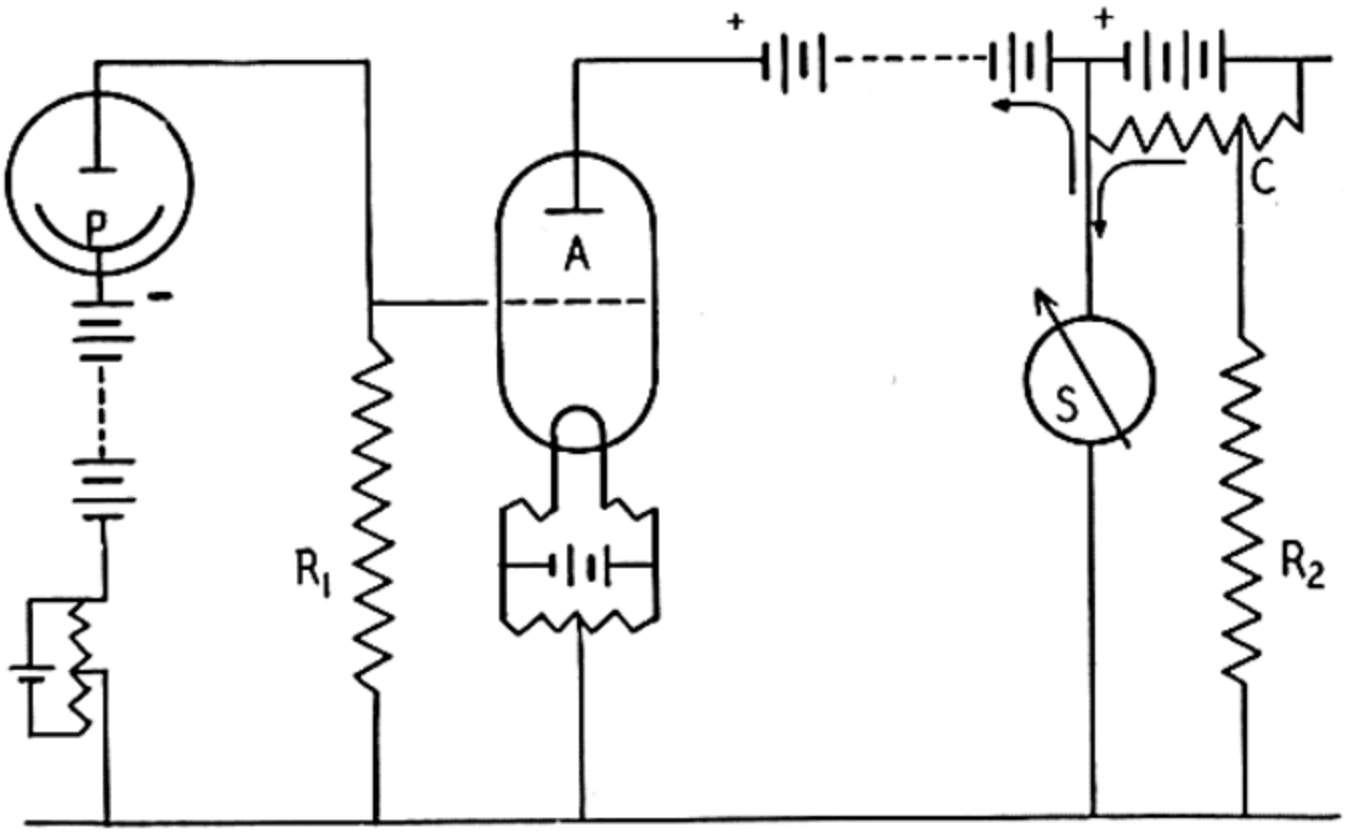

Fig. 28.—Photocell with amplifier and potentiometer compensation.

source is so constant that the different readings can be taken one after the other.† If this is not the case, two photoelectric cells of the same type

* In order to avoid too high amplification of the comparatively weak currents in vacuum photocells, the current can be intensified by means of so-called electron multipliers. The electrons emitted by the photocathode are accelerated by high voltage and impinge upon a metal plate from which they liberate a greater number of secondary electrons. These are subjected to the same process which may be repeated ten times or more. Thus the same purpose is achieved that is accomplished in gas-filled cells by the ionization of the gas, but without such disadvantages of this method as inertia, want of exact proportionality and danger of glow discharge (see Fig. 36). Electron multipliers or "photon multipliers" are now manufactured commercially.

† The absolute sensitivity of photoelectric cells of all kinds, even of vacuum emission cells, is in general not quite constant over longer periods of time. Hence measurements made at intervals of several days do not produce results of exactly comparable value.

(barrier layer cells or surface emission cells) must be connected in an opposite direction with the same galvanometer (Fig. 30). Thus, one of

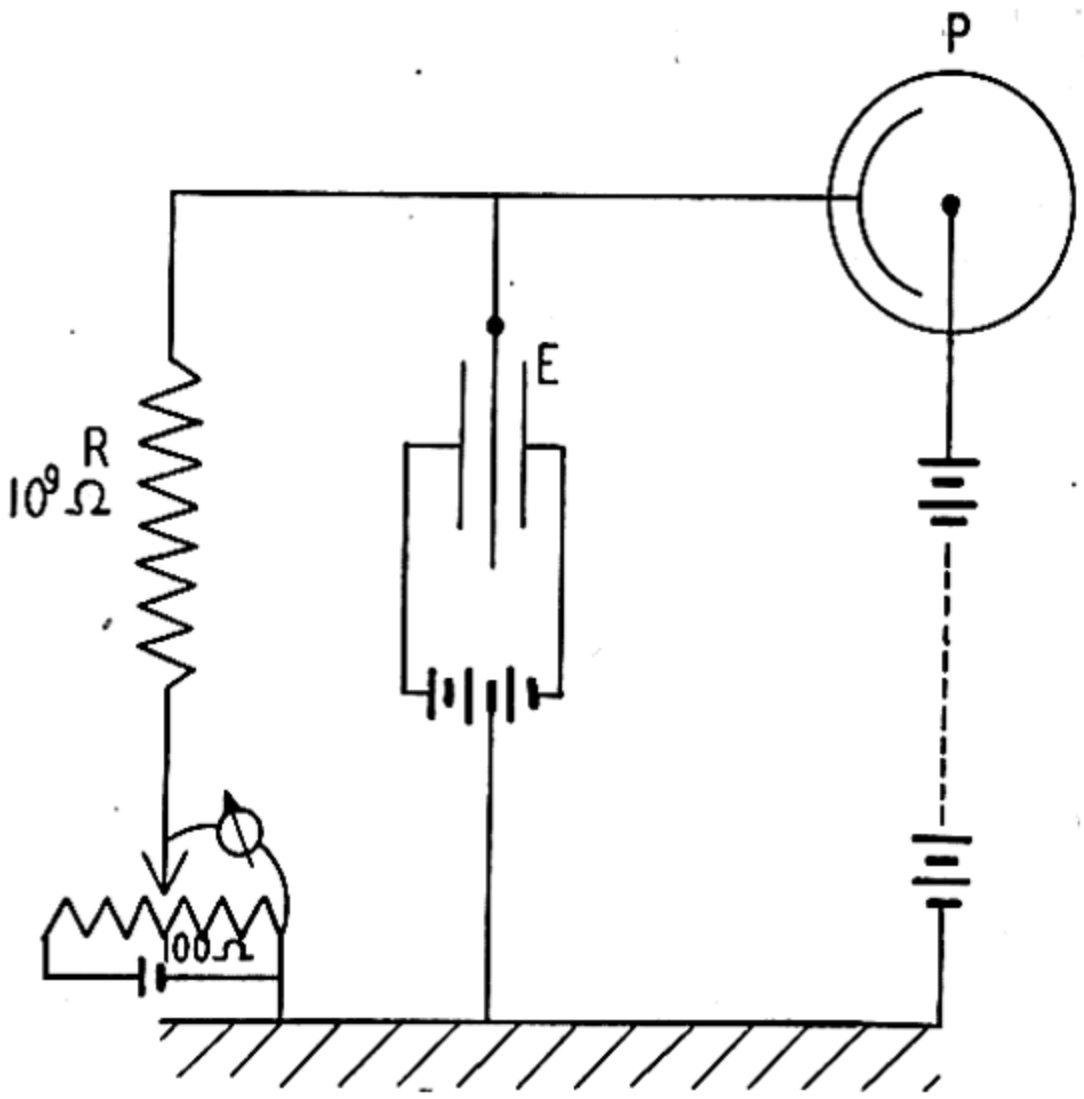

Fig. 29.—Photocell connected to a string electrometer for photometric work.

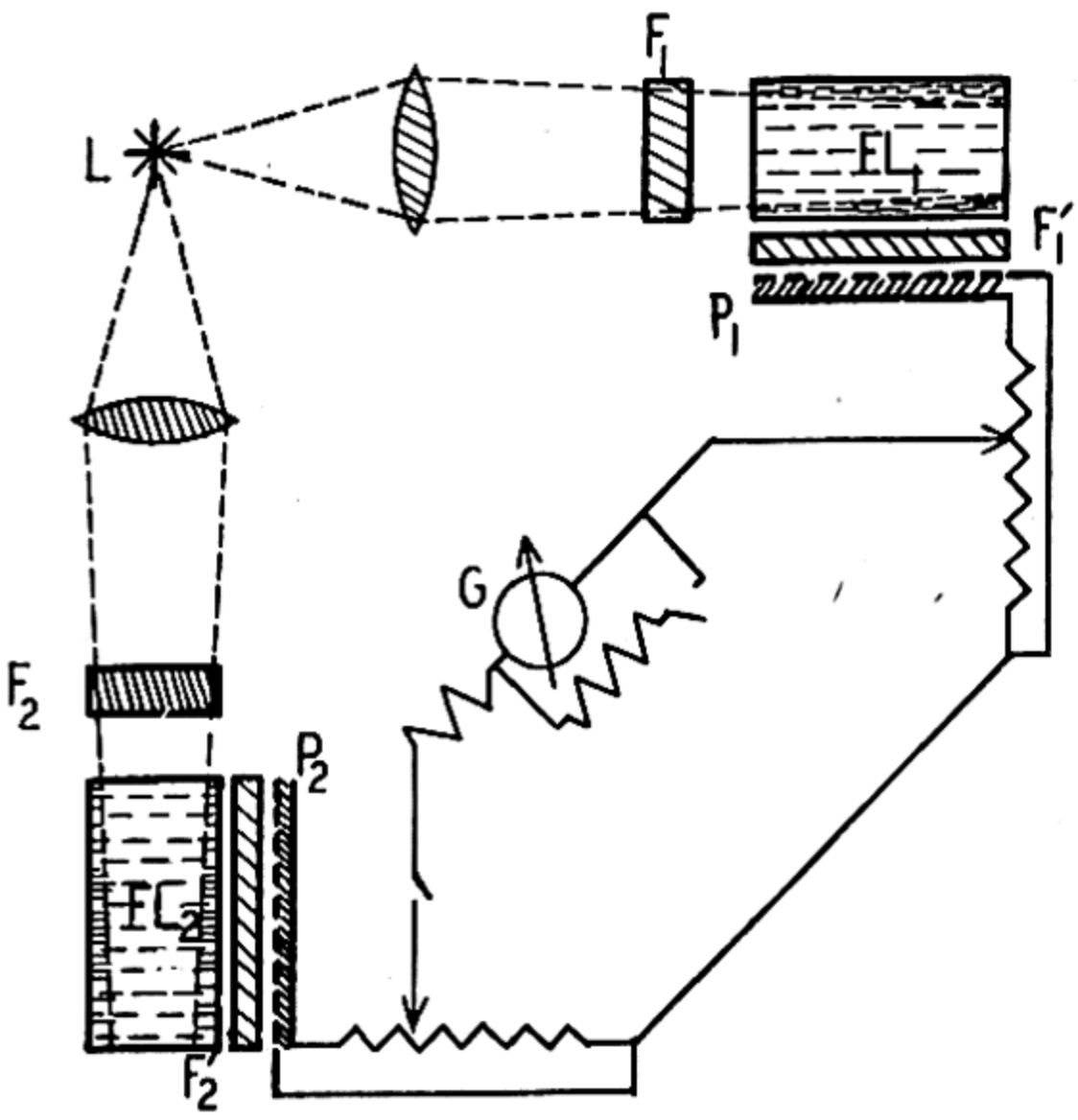

Fig. 30.—Two photronic cells in compensating circuit ("fluorimeter").

the two cells is illuminated by the fluorescent light source which is to be measured and the other by the standard source.* Exactly as in visual photometry the latter must be weakened until the two currents are equal and the galvanometer deflection is zero. This can also be attained by variation of voltage in one of the two photocell circuits (Fig. 30), but if such a method is applied a previous calibration of the photometer by means of light sources of known relative intensities is necessary.†

For photographic photometry a series of exposures of the standard source with various intensities has to be taken on the same plate and with the same time of exposure which has been used for recording the fluorescence light. After development the densities of the different photograms are determined and the intensity of the fluorescence found by interpolation.

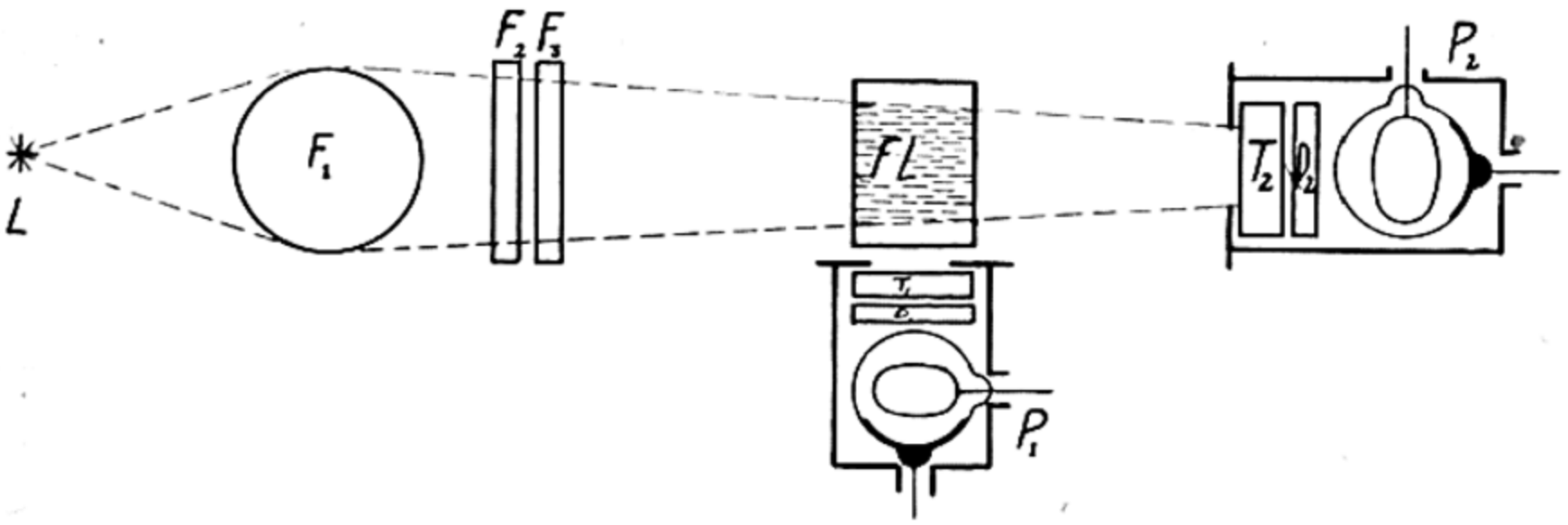

Fig. 31.—Bowens heterochromatic photometer for relative intensity measurements (observation sidewise).

In all photometric measurements on fluorescent material the crossed filter method should be applied, so that no diffused exciting light enters the photometer.

If the fluorescence intensity of a transparent substance (glass, liquid solution) is to be measured and the absorption of the exciting light is small, the observation is usually made "sideways." This method affords reliable results only for an absorption so weak that the fluorescence intensity is practically uniform across the whole area under observation. If the absorption becomes stronger and the fluorescence decreases along the

* In this case the standard need not be of the same nature (same fluorescence color) as the other sample; it is only necessary that it is excited by the same primary light source.

† In commercial fluorophotometers the compensating potentiometer is usually calibrated for direct intensity comparison. A detailed discussion of a great many different photoelectric photometer circuits and an exhaustive bibliography on this subject are to be found in an article by R. H. Mueller, *Ind. Eng. Chem., Anal. Ed.*, **11**, 1 (1939).

beam of the exciting light, the relative intensity of the fluorescence entering the photometer may be altered and the measurements may thereby become unreliable. With strongly absorbing solutions or with opaque material the measurement must always be carried out by "backward" observation (*e.g.*, Fig. 32).

It is to be emphasized that for all photometric work the light intensities to be compared must have identical color or spectral distribution* since the human eye as well as all photoelectric cells and photographic plates are more or less selective in their response to light of different wave-lengths. If the condition is not fulfilled, independent measurements must be made for different parts of the spectrum, using either light filters or spectrometers in combination with the photometer.

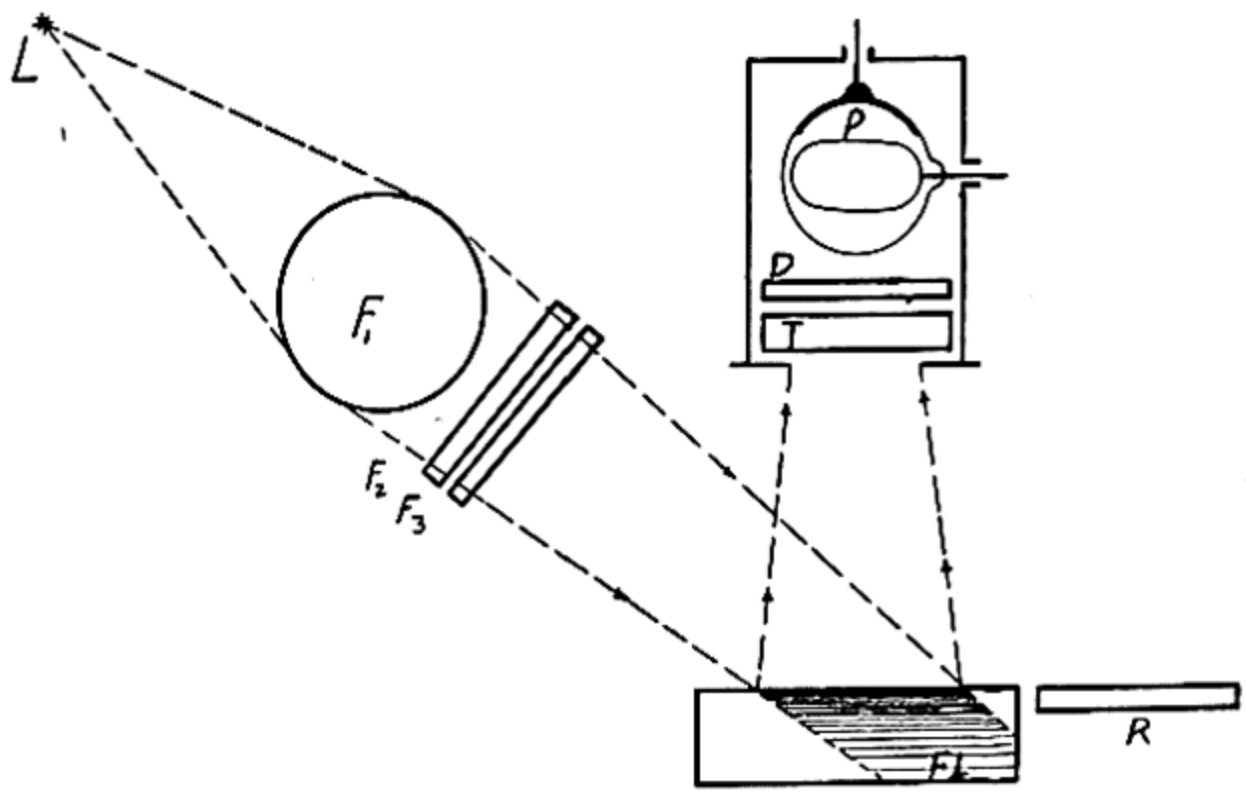

Fig. 32.—Bowens heterochromatic photometer for the determination of absolute fluorescence yield (observation backward).

The following method for "heterochromatic photometry,"† independently proposed by several authors,[11] has been applied lately by Bowen to the measurement of fluorescence yields.[12] It is based on the fact that the quantum yield Q of many fluorescent substances (dyestuffs in solution, uranyl salts, and others) is independent of the wave-length of the exciting light as long as Stokes' law is obeyed. If a fluorescent screen absorbs all incident radiation of any wave-length, the intensity of its fluorescence is

* This is by no means the same; two beams of light of very different spectral intensity distribution can produce the same color impression, and relatively small shifts in spectral distribution can make a very great difference in color.

† Heterochromatic photometry by means of the "flicker" method will hardly be useful for fluorescence analysis.

[11] A. Gyemant, *J. Optical Soc. Am.*, **12**, 65 (1926); W. Andersen and L. T. Bird, *loc. cit.*; G. R. Harrison and P. A. Leighton, *Phys. Rev.*, **38**, 899 (1931).

[12] E. J. Bowen, *Proc. Roy. Soc. London*, **A154**, 349 (1936).

proportional to the number of photons constituting the absorbed light. The wave-length of the fluorescence is always the same, and therefore, its action upon a photoelectric cell depends only on its intensity. The fluorescence of this "integrating screen" is excited by the fluorescence of the substance, of which the fluorescence yield is to be determined. Bowen's integrating screens were made of uranyl sulfate crystals suspended in pure paraffin or of aesculin in aqueous solution. The former begins to absorb strongly at about 4100 and the latter at about 4000 Å; hence they are only useful for the measurement of violet or U.V. light. A solution of rhodamine B dissolved in solid glyptal varnish responds equally well to all wave-lengths from the *D* lines to the far ultraviolet with a strong orange-red fluorescence,* and would extend the use of this method to almost every fluorescent emission. Bowen's apparatus for the measurement of the relative fluorescence yield of solutions is reproduced in Fig. 31. The photoelectric cells P_1 and P_2, measure the fluorescence intensity I and the light absorption A of the solutions, respectively. T_1 and T_2 are the integrating screens and D_1 and D_2 are light filters protecting the photoelectric cells against any light which does not come from the integrating screens. F_1, F_2 and F_3 are filters selecting one line of the spectrum emitted by the mercury arc L (see Table VII). The final value $Q_r = \frac{I}{A}$ is the relative quantum yield of fluorescence.

It is much more difficult to obtain absolute values of fluorescence yields. As a matter of fact only very few experimental results are to be found in all of the literature, and most values of fluorescence yields which have been published by different authors are reductions of relative measurements by comparison with one of the few directly obtained yields.

For the determination of the absolute value of the fluorescence yield, the luminous intensity emitted by unit surface of the fluorescent sample in a given direction (*e.g.*, normally to the surface) must be compared with the intensity diffused under the same angle by a perfectly white and matt surface, when both are struck by the same primary monochromatic light. From these values the total intensity emitted or diffused in all directions is found by integration over the whole sphere. For a transparent fluorescent solution this value is according to Lommel's law four times as large as that which would be found by application of Lambert's cosine law if both intensity measurements were made in a direction perpendicular to the surface (compare page 23).

The first experiments of this kind were performed by Vavilov for a

* According to Marden and Beese, rhodamine fluorescence is not excited by light of wave-length below 3000 Å. This is certainly not true for the rhodamine B solutions mentioned above.

number of liquid dyestuff solutions.[13] He worked with a visual photometer and since the (exciting) light diffused by the white surface and the fluorescence were necessarily of different color he had to calibrate his photometer for every color by comparison with the intensity of a light source of known spectral intensity distribution (Hefner candle). According to Vavilov's own statement these measurements cannot claim a high degree of accuracy. Nevertheless, almost all other data published on the fluorescence yield of dyestuffs and some other solutions are derived from these values.

Bowen[14] has determined the absolute fluorescence quantum yield of anthracene dissolved in hexane by comparison with the light diffused from a magnesium oxide surface using his heterochromatic photometer as shown in Fig. 32. With the help of this value a great many relative measurements made with the apparatus of Fig. 31 could be converted into absolute yields. Some of them are given in Table IV.

3. Spectroscopy

The human eye is a very sensitive instrument for the discrimination of color, and different authors give rather elaborate methods for defining a color by its hue and saturation. It is even possible that in some cases a difference of color is recognized more easily by direct vision than by examination of the corresponding spectrograms. Nevertheless, the only reliable way to gain an exact knowledge of the nature of a luminescence radiation is to examine it with a spectroscope, or rather by means of a spectrograph, since this permits better facilities for wave-length measurements and extends the observation into the U.V. region. By far the most numerous luminescence spectra consist of relatively broad bands; therefore, high dispersion is not needed and should be avoided inasmuch as it is opposed to the large aperture which is essential in many cases because of the small intensities. For this reason comparatively wide slits may be used. For most purposes a small quartz spectrograph like the Hilger-E 37 is quite sufficient and only if the luminescence spectrum reaches beyond 5500 Å toward longer wave-lengths does the dispersion become too small so that a glass spectrograph is required.

For light of wave-lengths larger than 4500 Å, the photographic plates must be sensitized; orthochromatic, panchromatic, and special spectroscopic plates are on the market.* Panchromatic plates are in general much slower in the U.V. region than are unsensitized plates. Therefore they should be used only if they are really needed. All sensitized plates

* For sensitization for short wave-length U.V. see page 158.

[13] S. I. Vavilov, *Z. Physik*, **22**, 266 (1924).
[14] E. J. Bowen and D. Norton, *Trans. Faraday Soc.*, **35**, 44 (1939).

have a more or less irregular spectral distribution of sensitivity, often with several maxima and minima. Hence an emission band which is in reality quite continuous may seem on a spectrogram to consist of several narrow bands separated by dark intervals. If the sensitivity of the plate for all parts of the spectrum is not ascertained by the somewhat complicated methods of quantitative spectrographic photometry, at least a series of spectra of a tungsten filament lamp should be taken with different time exposures. These will show qualitatively the response of the plate to light of different wave-lengths.

Some commercial spectrographs are fitted with a wave-length scale which can be reproduced on the plate. Though not of the highest precision this scale is very useful and quite sufficient in most cases. Otherwise a

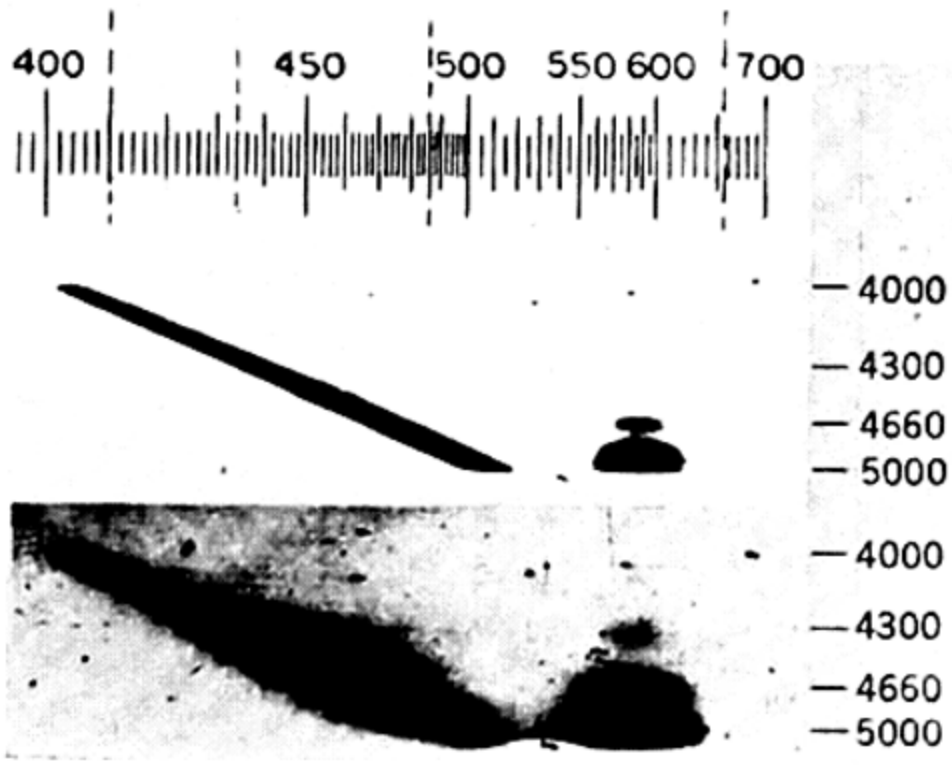

Fig. 33.—Method of crossed spectra for determination of exciting wave-lengths for ZnCdS(Mn) phosphor (Kroeger).

comparison spectrum must be taken on each plate and here again the mercury arc spectrum is simplest and in general quite satisfactory.

In order to find the excitation spectrum, that is, the spectral region by which a given substance may be excited to luminescence, the following method has been recommended independently by different authors:[15] a transparent film coated with a thin layer of the fluorescent substance is placed in a spectrograph immediately in front of the photographic plate, from which it is separated only by a thin screen transmitting the fluorescent light, but opaque to the exciting radiation. After development the plate is blackened exclusively at the spots where the fluorescent material had been excited by the incident light, the density of the blackening depending upon the intensity of the fluorescence.

[15] G. Heine and M. Pirani, *Z. tech. Physik*, **14**, 319 (1933); J. W. Marden and N. C.

In order to determine whether different emission bands are excited in one substance by incident light of different wave-lengths,* the method of crossed spectra was introduced by Stokes. A narrow continuous spectrum is projected upon the luminescent surface. This is viewed through a spectroscope with its slit perpendicular to the slit of the first spectrometer and deviating the spectrum of the exciting light and the fluorescence radiation. In Fig. 33 (upper part) the oblique band on the left side is the continuous spectrum of the twice deviated exciting light, reaching from 4000 Å to a little beyond 5100 Å. The horizontal stripes on the right hand are produced by one and the same narrow fluorescence band of a ZnS(Mn) phosphor at 5650 Å. It is excited by light of 5000 and of 4700 Å. In the lower, much overexposed photogram, a third excitation region can be discerned corresponding to a primary radiation of 4300 Å.

For phosphorescent material the excitation spectrum of the afterglow is frequently quite different from the fluorescence excitation spectrum, even if the emission band is the same in both processes. If a continuous spectrum is projected upon the phosphorescent surface, the luminescence may have a certain intensity distribution along the primary spectrum as in Fig. 41.[16] After the removal of the exciting radiation the luminescence disappears in all regions where it was excited as fluorescence alone. Only in restricted regions, which sometimes are confined to narrow bands, is a persisting afterglow observed, while parts of the irradiated surface lying between these bands appear perfectly dark.[17a]

4. Phosphoroscopes and Fluorometers

The theory of the decay of luminescence after the excitation is stopped is not yet of great interest for practical applications, as has already been mentioned on page 35. But measurements of the time during which the luminescence retains a certain intensity may be very important. The periods after which the intensity has decreased to *1/2* or *1/e* of its initial value J_0 (so that $J = 1/2\, J_0$ or $1/e\, J_0$) are called the half life ϑ and the mean life τ of the luminescence, respectively. In order to determine τ for a long afterglow, one has only to measure its intensity at regular intervals

* A few cases of this type are known among dyestuffs (*e.g.*, Meldola blue) in solution as well as among inorganic phosphors. But in most of these cases the exceptional behavior is probably due to the fact that they are composed of two different and independently excited substances.

[16] F. A. Kroeger, *Physica*, **7**, 369 (1939).

[17a] P. Lenard, F. Schmidt and R. Tomaschek, *Phosphoreszenz und Fluoreszenz* (*Handbuch der Experimentalphysik., Vol. 23/1* and *2*) Akademische Verlagsgesellschaft, Leipzig 1928.

by one of the methods of section 2 and to draw a curve representing J (or log J) as a function of the time t. For luminescence with a lifetime below $\tau = 1$ sec. a number of methods have been developed for practical use. These may be divided into three classes, each having its individual advantages and special fields of application.

1. The sample is alternately irradiated and observed at regular time intervals. The first instrument constructed for this purpose was called a phosphoroscope by its inventor, E. Becquerel [17b] (Fig. 34). The phosphor is placed between two rotating discs with alternating opaque and light transmitting sectors mounted on the same axis. The two discs are set with respect to each other so that a transparent sector of the first disc permits the exciting light to impinge on the sample, while an opaque sector of the second disc hides it from the observer. When the luminescent substance becomes visible through an opening in the second disc, the exciting light is intercepted

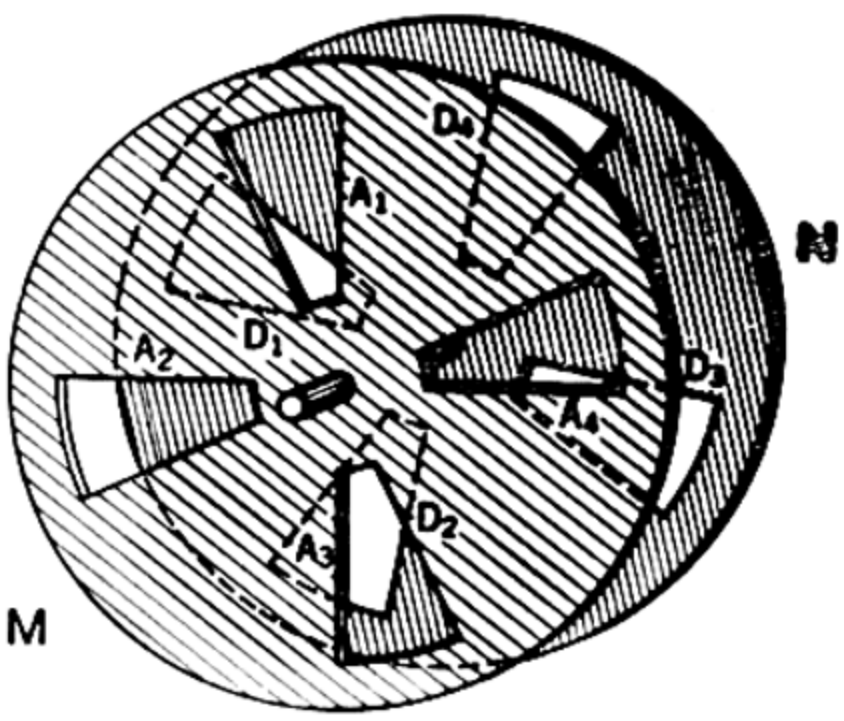

Fig. 34.—Becquerel phosphoroscope (after Becquerel's original drawing).

by an opaque sector of the first disc. By changing both the angle between the corresponding sectors of the two discs and the speed of rotation, the time which elapses between the end of the excitation and the moment of observation can be varied within certain limits. A device still simpler, but based on the same principle, is to have the phosphorescent material fixed on a cylinder rotating inside of a coaxial cylindrical tube at rest; the tube is opaque except for two slits at different points of the circumference, the one serving for the irradiation and the other for the observation of the phosphor. In another phosphoroscope the luminescence is excited by means of an electric spark which by some mechanical device is started a short time before the open segment of a rotating disc unmasks the phosphor.[18] The same meth-

[17b] E. Becquerel, *La lumière, ses causes et ses effets.* Firmin Didot, Paris 1867.
[18] P. Lenard, *Ann. Physik*, **46**, 637 (1892).

ods can also be used if the phosphorescence is not excited by a light beam but by cathode rays, though the instantaneous release of a cathode ray beam requires a somewhat more complicated setup.[19] No apparatus of the above types, however, will be sufficient for the measurement of lifetimes below 10^{-4} sec. One can go much farther (down to 10^{-8} and even 10^{-10} sec.) by replacing the mechanical devices by nonmechanical light shutters.* Such shutters are electromagnetic Kerr-cells which are operated by high frequency alternating potentials and are placed between crossed Nicol prisms,[20] or ultrasonic waves in a liquid[21] or in crystalline[22] quartz by which the transmitted light is deviated into "spectra of higher order" during each period of maximum amplitude of the ultrasonic wave. These methods will never be used outside of specially equipped physical laboratories and therefore shall not be discussed here at length.

For quantitative determinations the intensity of the phosphorescence has to be measured by means of a photometer, at the present time usually a photoelectric cell, for different time intervals between excitation and observation. If only the order of magnitude of τ is wanted, it may be deduced from these intensity measurements by the primitive method used by Becquerel himself,[23] namely by plotting the intensities τ against the time elapsed between full illumination (sector of first disc quite open) and full observation (observation sector quite open). With certain types of Becquerel phosphoroscopes, as with Becquerel's own construction and all Kerr-cell fluorometers as well, this may lead to rather incorrect values, sometimes twice as large as the true ones.[24] However, the corrections to be applied are of little importance if the observation sector is a narrow slit, so that the intensity of the luminescence does not decay appreciably during the time of its passage in front of the photocell, and if the illuminating sector's aperture and the rotation speed are kept constant, the time between excitation and observation being changed only by varying the angle between the two sectors.†

2. The luminescence is continually excited at a certain spot and the

* An apparatus constructed for this purpose is called a fluorometer, a name which, therefore, should not be employed for fluorophotometers.

† With much more brilliant light sources and sensitive photometers these conditions can now be attained much more easily than in the time of Becquerel, who, for the sake of a gain in luminosity, resorted to his less favorable arrangement.

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[19] R. B. Nelson, R. P. Johnson and W. B. Nottingham, *J. Applied Phys.*, **10**, 335 (1935).

[20] E. Gaviola, *Z. Physik*, **42**, 853 (1927); W. Szymanowski, *ibid.*, **95**, 440 (1936).

[21] O. Maercks, *ibid.*, **109**, 685 (1938).

[22] L. A. Tumermann, *J. Phys. U. S. S. R.*, **4**, 169 (1941); H. R. Briggs, *J. Optical Soc. Am.*, **31**, 518 (1941).

[23] E. Becquerel, *Ann. chim. phys.*, **62**, 5 (1861).

[24] A. Delorme and F. Perrin, *J. phys. radium*, **10**, 177 (1925).

luminescent material is removed from the spot at high speed. This method has been used to very great advantage for luminescent gases, especially when they are ionized and accelerated by an electric field as in canal rays. Thus W. Wien measured lifetimes of excited atoms or molecules of the order of 10^{-8} sec. For solid or liquid substances the simplest method is to have the material fixed on a rotating disc, if possible along a whole circle near the rim of the disc. Under these conditions a luminescent circle will originate at the spot where the excitation takes place and show the complete decay curve simultaneously if the rotation of the disc has an adequate

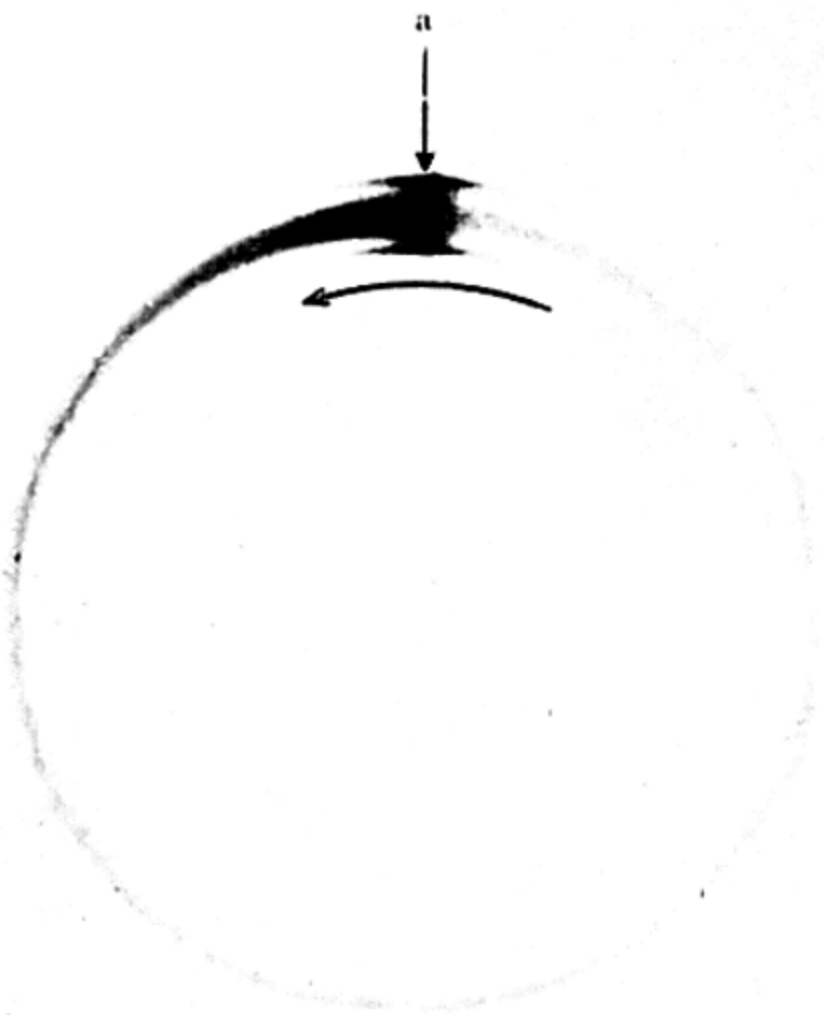

Fig. 35.—Rotating disc phosphoroscope (from a paper by Buenger and Flexig). Luminescence of a BaClTl phosphor. a: "Timeless" fluorescence. At first quarter of left side: fast decaying afterglow. Remnant part of the circle: slowly decaying phosphorescence.

angular velocity (Fig. 35). Not only is it possible to measure lifetimes $\tau \approx 10^{-5}$ sec. by this method, but if the phosphor covers the whole circle, it can also be applied to the determination of lifetimes between 0.5 and several seconds which can hardly be investigated by a phosphoroscope with intermittent excitation.[25] For small values of τ the method can be improved by viewing the luminescence reflected by a rotating mirror so that the light emitting point is drawn out into a band. In this case the excitation must again be produced by a spark which is started once at

[25] R. W. Wood, *Proc. Roy. Soc. London*, **A93**, 362 (1921); W. Buenger and W. Flexig, *Z. Physik*, **67**, 42 (1931).

every revolution of the mirror; the lower limit for this method is $\tau = 10^{-6}$ seconds.[26]

3. The luminescence light produces an electric current in an emission photocell, which after amplification acts upon one pair of electrodes of a cathode ray oscillograph (Fig. 36). The other pair of electrodes of the oscillograph is operated by an alternating potential of about 50 or 60 cycles per sec. By means of rotating sector discs in front of the primary light source, the luminescence is excited ten times per second during

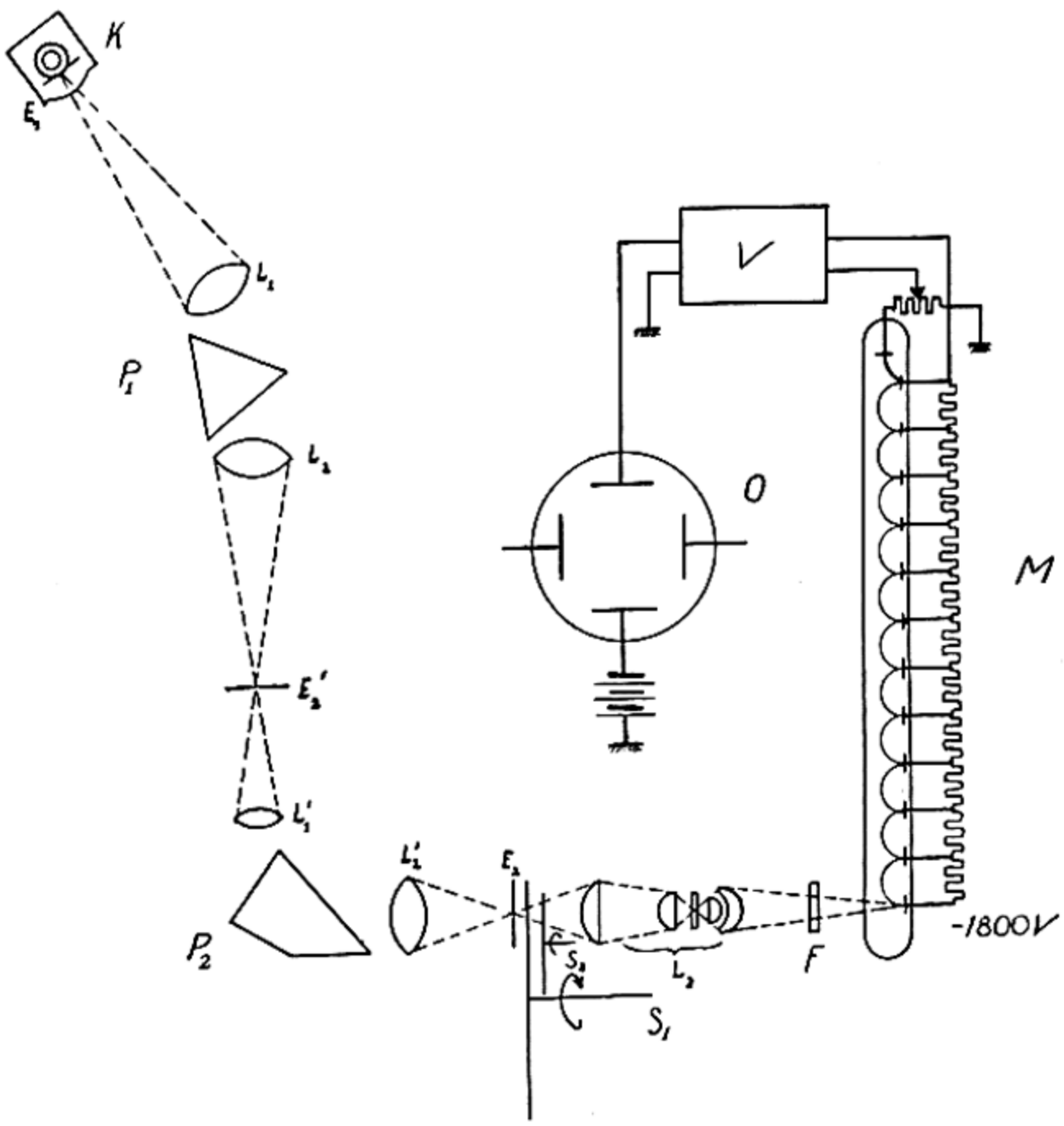

Fig. 36.—De Groot's fluorometer with electron multiplier and cathode ray oscillograph.

periods of 10^{-2} sec. During these periods of irradiation the luminescence increases to its highest intensity, producing a maximum deflection of the oscillograph spot. During the period following the irradiation the luminescence intensity drops to zero. After 0.1 sec. the same cycle is started once more and the figures produced by each cycle on the oscillograph screen coincide exactly if after 0.1 sec. the auxiliary alternating potential applied to the oscillograph plates passes again through zero

[26] S. I. Vavilov and V. L. Levshin, *Z. Physik*, **35**, 920 (1926).

(Fig. 37). For values of τ between 10^{-4} and 10^{-2} seconds the total intensity time curve of the growth and decay of the luminescence is thus rendered visible by the oscillograph and can be retained on a photographic plate[27] (Fig. 6, p. 15). The same method can be applied, with slight modifications, for luminescence excited by cathode rays.

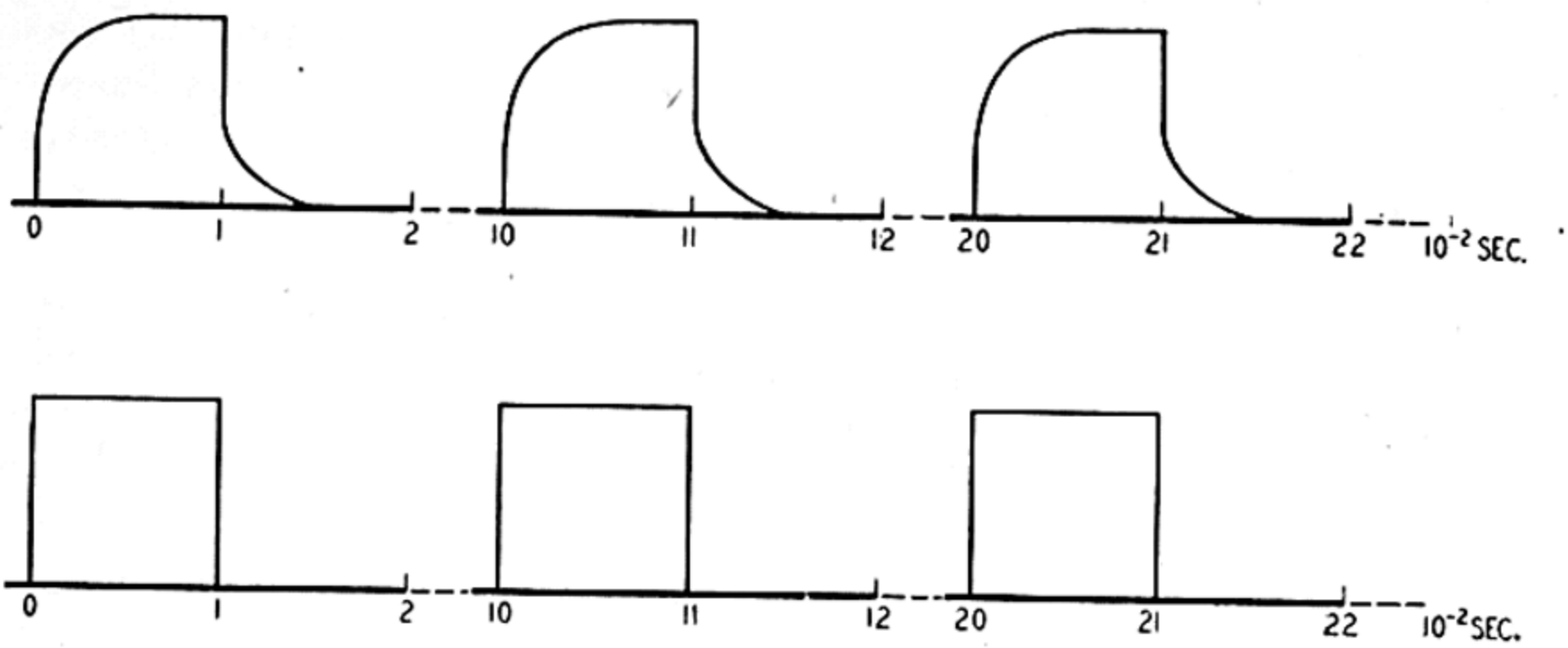

Fig. 37.—Schematic curves obtained with De Groot's fluorometer.

5. Fluorescence Microscopy

In fluorescence microscopy an object is made visible not by the light from a primary source which it transmits or reflects, as in ordinary microscopy, but by the fluorescence which it emits when excited by incident light, cathode rays or x-rays. Regarding the specific technique of this method little is to be added to the contents of the first two paragraphs of this chapter. The microscope itself does not differ from any other type of microscope. It need not be equipped with quartz lenses as long as visible fluorescence light is to be observed. And, exactly as in ordinary microscopes, the objects are viewed "forward" (light incident from below, if the microscope is in vertical position) or backward (light incident from above). The second method alone is possible with opaque objects. It has the great advantage that no thin sections of the object under observation are needed. Light sources, compensated filters, reflectors, and lenses must be chosen according to the rules given in the foregoing paragraphs. It seems that so far, the near ultraviolet, as transmitted through a Wood filter, has been used almost exclusively for excitation, but there is no reason why in special cases light of wave-lengths below 3000 Å should not be more efficient.

As to the question of whether high or low magnification is preferable in fluorescence microscopy, the champions of the method give rather contra-

[27] W. De Groot, *Physica*, **6**, 275 (1939).

dictory answers: Danckwortt advocates the first,[28] Haitinger[29] the second. The alternate choice depends, of course, mainly on the problems under consideration. It also depends very much on the light intensities which are available. For a microscope of high magnifying power it is not the total light output of the primary light source which is important, but only its brightness, the intensity per sq. cm. Hence for the violet and near U.V. region the carbon arc,* and for the far U.V. region the high pressure mercury arc may be most suitable. Haitinger, who made fluorescence microscopy his specialty, recommends an arc between iron electrodes, burning at 5 amp. and 40 volts in a closed metal chamber with only a small aperture for the exciting light beam.

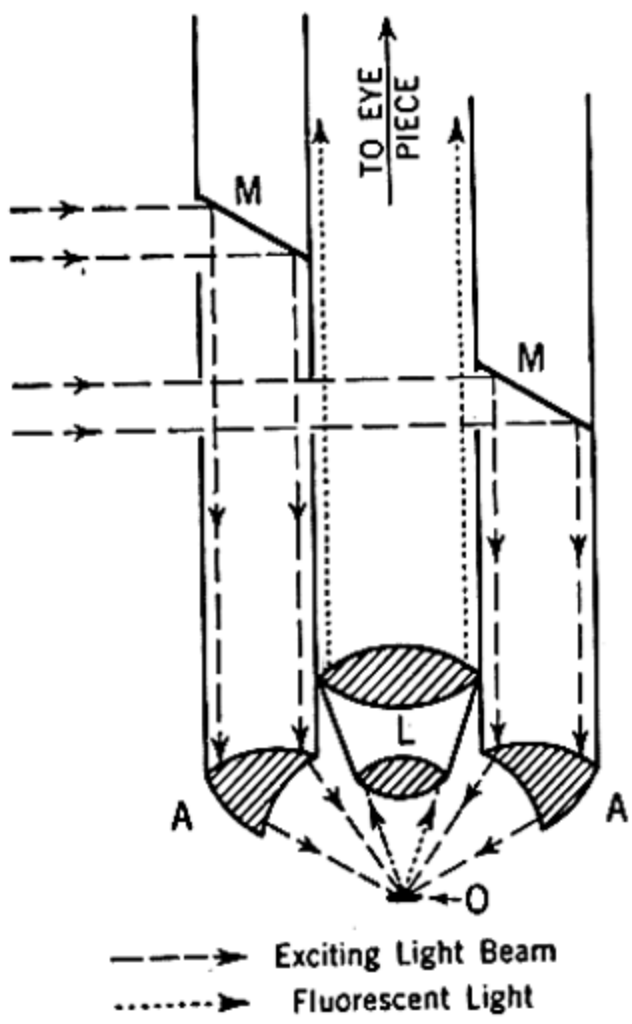

Fig. 38.—Fluorescence microscope (Haitinger).

If the focal length of the microscopic objective allows sufficient working space, the primary light can be concentrated from above upon the object at an angle of 45° by means of a concave mirror. This is no longer possible with high magnifying power and especially if immersion systems are used. For this purpose different kinds of vertical illuminators exist for ordinary microscopes. For fluorescence microscopy the arrangement sketched in Fig. 38 is especially designed to combine high magnification and great luminosity: *M* is an annular mirror reflecting the U.V. light toward the likewise annular condenser lens *A* which concentrates the exciting beam upon the object *O*; the object is viewed through the objective lens *L*. It is to be kept in mind that all mirrors and reflectors for the exciting light must be front surface aluminized and not silvered. If possible, the microscope objective should be protected against reflected radiation by a filter not transmitting U.V. light.† Any

* For strongly fluorescent objects and not too high magnification even a low voltage high amperage concentrated filament microscope lamp emits sufficient ultraviolet radiation.[30]

† Normal microscopes equipped for fluorescence microscopy with a front aluminized mirror and the necessary filters are supplied by the Spencer Lens Company and other optical firms.

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[28] P. W. Danckwortt, *Luminescenzanalyse*, Akademische Verlagsgesellschaft, Leipzig 1928 (4th ed. 1940).

[29] M. Haitinger, *Fluorescenzmikroskopie*. Akadem. Verlagsgesellschaft, Leipzig 1938.

[30] O. W. Richards and D. K. Miller, *Am. J. Clin. Path.*, **11**, techn. suppl. 5, 1 (1941).

fluorescence produced in the lens system (Canada balsam, etc.) would appear as a glare masking the fluorescence image of the object. As for the use of a $CuSO_4$ filter in the path of the primary beam, we refer to page 43.

The objects to be examined under the fluorescence microscope are of two different types. Either they are luminescent by themselves, or they must be stained by means of some fluorescent solution exactly as preparations are stained by different dyestuffs for ordinary microscopic research. Haitinger gives a long list of dyestuffs and other organic compounds which he calls fluorochromes and which are useful for this purpose. As a matter of fact, any strongly fluorescent material apt to be adsorbed by, or dissolved in, the substance under investigation may be employed. To a certain degree the choice of the "fluorochrome" is determined by the nature of the substance, its acidity, its body color, the natural fluorescence of parts of the substance, etc. The following are the fluorochromes which in general give the best results: choriphosphine O, aurophosphine, thioflavin, thiazole, yellow g, berberine sulfate, trypaflavin, primulin yellow, fluorescein, and eosin. The dyestuffs are dissolved in water, usually in concentrations from 0.1 to 1 mg./cm.^{3}, and the substance is soaked in the solution for a period of several minutes.

For cathode ray excitation of mineral phosphors under the microscope a simple device has been developed by Gallup.[31] In a small cell, connected to a vacuum pump, cathode rays are produced by the high frequency discharge of a spark coil. The fluorescence is observed through a flat cover glass fitted to the rim of the cup-shaped cell by a greased vacuum seal. The cell can be clamped to the stage of a normal microscope with a 16 mm. objective. The purpose of the apparatus is to select microcrystalline material for cathode ray fluorescent screens under excitation conditions similar to those in oscillographs and other cathode ray tubes.

The fact that in fluorescence microscopes the objects are self-luminescent and not viewed by means of reflected or transmitted light does not make a great difference in the theoretical maximum resolution which is in both cases defined by the wave-length of visible light and the numerical aperture of the objective. But if the fluorescence intensity is strong enough, the method might be used for ultramicroscopy as with dark field illumination. Without showing any details of form or structure, individual objects of diameters below the limits of resolving power might still be located and their movements observed.

[31] J. Gallup, *J. Optical Soc. Am.*, **6**, 213 (1936).

CHAPTER IV.

LUMINESCENT MATERIALS AND THEIR PROPERTIES

1. General Survey

For two reasons it is difficult to define the lim between luminescent and non-luminescent substances. The problems are of intensity on one side and of purity on the other. A substance usually classified as "non-luminescent" may show, under strongest excitation, a very weak emission observable only with eyes fully adapted to complete darkness or by over-long photographic exposure. Such cases are of small practical interest. We shall list a material as luminescent only when its emission can be observed without difficulty under normal conditions. Even in accord with this restriction many substances seem to be luminescent, although the luminescence is no property of the substance as such, but is due to small, and often, unknown traces of impurity.

Thus so-called pure distilled water shows an easily visible violet fluorescence when it is irradiated with light of the near U.V. region.[1] By repeated distillation of the water the fluorescence becomes weaker, though it seems to be impossible to make it disappear completely. A similar behavior is characteristic for many other liquids like alcohol, benzene, glycerin,[2] etc.* On the other hand, the moistened surface of many non-colored inorganic salts emits a bright blue fluorescence and phosphorescence under black light excitation.[3] Among these salts are several like silica which are not soluble in water and which are not excited to any luminescence by black light when their surface is dry. Diamonds of the purest quality are frequently not fluorescent. Other samples show a strong blue or yellow fluorescence and some are even phosphorescent with a rather long lasting afterglow. Though this light emission is certainly not a characteristic property of the carbon atoms in the diamond lattice, it is not yet possible to ascribe it to any known source.

* After distillation *in vacuo* ethyl alcohol becomes fluorescent only when it has been exposed for some time to the influence of atmospheric air. Dudd contends that even some of the most brilliantly fluorescent dyestuff solutions, like an aqueous uranin solution, become non-fluorescent after repeated recrystallization of the dyestuffs and regain their luminescence only after exposure to the atmosphere. However, this statement has never been corroborated by any other author and can not be accepted as correct for the time being.

[1] A. Carrelli, P. Pringsheim, and B. Rosen, *Z. Physik*, **51**, 511 (1928).

[2] S. I. Vavilov and L. A. Tumermann, *ibid.*, **54**, 270 (1929).

[3] J. Ewles, *Trans. Faraday Soc.*, **35**, 119 (1939).

Numerous substances which are not photoluminescent or only very slightly photoluminescent are excited to strong fluorescence or phosphorescence by cathode ray bombardment or x-rays. It must be kept in mind, however, that by some kind of chemical reaction this irradiation itself creates new impurity centers, which become the carriers of the luminescence. It is a well-known fact that many colorless inorganic salts acquire color under the impact of cathode rays or x-rays. This colored modification is in many cases photoluminescent and "thermoluminescent." Similar effects are sometimes produced by short-wave ultraviolet light with inorganic crystals as well as, more frequently, with organic compounds. Cyclohexane, for instance, was supposed to be fluorescent under the action of ultraviolet light until Padmanabhan[4] proved that this fluorescence appeared only after a period of illumination and was due to an impurity produced in pure cyclohexane by a photochemical reaction.

Concerning the nature of luminescent substances and their characteristic properties, the following rules in general prevail. In a condensed state (liquid or solid) practically no pure elements and very few simple compounds are luminescent.*

Most substances with a strong luminescence are white or at least not deeply colored. Though many dyestuffs show a brilliant fluorescence, it is not in contradiction with the rule, since the fluorescence yield of these compounds is high only in very dilute solutions.

Many substances become luminescent, or their luminescence is strongly increased, when they are cooled down to liquid air temperature. Heating to a certain upper limit, which lies usually between 100 and 400° C., destroys the fluorescence in almost every case.

Liquid solutions are practically never phosphorescent, though in very viscous liquids a short afterglow may sometimes be observed.[7]

In the solid state many compounds show an afterglow easily observable with a phosphoroscope or even lasting several seconds.[8] However, phosphorescence persistent over many hours, and "frozen in" at low temperatures over days and weeks, is almost exclusively a property of "crystal phosphors" activated with small traces of an impurity.†

* The only exception known so far is the cathodo- and canal ray luminescence of solid nitrogen at the temperature of liquid hydrogen. The photoluminescence of yellow phosphorus[5] mentioned by Randall is at least doubtful.[6]

† The only exception to this rule, of which we are aware, is the platinocyanides. At room temperature their luminescence is of very short duration. When immersed

[4] R. Padmanabhan, *Mem. Ind. Inst. Sci.*, **A2**, 209 (1935).

[5] L. Vegard, *Physik. Z.*, **25**, 685 (1924); T. C. McLennan and J. Shrum, *Proc. Roy. Soc. London*, **A106**, 98 (1924).

[6] J. T. Randall, *Trans. Faraday Soc.*, **35**, 2 (1939).

[7] S. Boudin, *J. chim. phys.*, **27**, 285 (1930); H. Kautsky, *Chem. Ber.*, **68**, 153 (1935).

[8] E. Wiedemann and G. C. Schmidt, *Ann. Physik*, **58**, 103 (1896).

The light emission capacity of many substances which are luminescent under normal conditions is diminished or totally suppressed by the presence of some other substances. Oxygen, the halogens both in the molecular and the ionic state, in other cases metal such as iron or nickel, or organic compounds such as aniline, phenol, resorcinol or pyrogallol, have such a "quenching" effect, but the same substance which inhibits the luminescence in one case may be quite inefficient in another.[10*] Since in a solution the molecules of the solvent may act simultaneously as quencher, the fluorescence yield of a given substance may have very different values in different solvents. In general, other conditions being equal, the quenching effect is the stronger, the longer the lifetime of the excited system. Hence the afterglow of a luminescent substance is inhibited by much smaller concentrations of a quencher than a fluorescence of short duration.

Luminescent substances can be divided into three main classes:

1. *Organic compounds.*—Among these are not only many substances of well-known chemical composition, but numberless complex matters produced by nature or by human craftsmanship. Almost every part of the human or animal body is fluorescent, skin, tissues, fat, nails, teeth, hormones and vitamins, milk and eggs; also leaves, fruits, plant extracts, flour, oils, resin, wood pulp, cellulose, paper, silk, etc. Even where the chemical composition of such substances is known in principle, they are never pure in the sense of fluorescence analysis, and relatively seldom the real carrier of the luminescence can be traced as an essential and constituent part like chlorophyll in leaves or riboflavin in milk. In many other cases the fluorescence may be perfectly accidental and not connected at all with the nature of the substance.

2. *Pure inorganic compounds*, of which only a very restricted number is known.

3. *Inorganic crystals and glasses activated by inorganic impurities.*—In this class it is once more useful to distinguish between synthetic products of well-known and carefully selected composition and natural minerals.

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in liquid air, however, they are able to store up a part of the excitation energy over a considerable period. The phenomenon of "frozen-in phosphorescence" was discovered by Dewar on barium platinum cyanide.[9]

* For instance, bromide ions are very efficient quenchers for quinine sulfate, they have little influence upon the fluorescence of an aesculin solution and they strongly increase the fluorescence of thallous sulfate, all in aqueous solution. On the other side the thallium fluorescence is quenched by ferrous ions. Traces of ethyl alcohol quench the fluorescence of uranyl sulfate in H_2SO_4, while uranin dissolved in ethyl alcohol yields a most brilliant fluorescence.

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[9] J. Dewar, *Chem. News*, **70**, 252 (1894).

[10] G. K. Rollefson and R. W. Stoughton, *J. Am. Chem. Soc.*, **61**, 2634 (1939); **62**, 2264 (1940); **63**, 1517 (1941); W. West and W. E. Miller, *J. Phys. Chem.*, **8**, 849 (1940).

With regard to the luminescence of minerals the remarks made about natural organic compounds could be repeated almost verbatim. Synthetic chemical compounds of more or less doubtful purity take an intermediate position between these two classes.

Within the scope of this book it is not possible to give a list, even tentatively complete, of all luminescent substances of well-defined chemical composition, though such a list, based on the most recent results and not repeating over and again old erroneous assertions would be very useful.* On the other hand it would be of rather doubtful value to enumerate all qualitative observations concerning fluorescent substances, as long as these observations do not lead to anything beyond the knowledge that these materials or even only certain samples of them can be excited to fluorescence.

In the following sections and in the tables at the end of the volume there is made a rather restricted selection of such luminescent substances as seem to be of special interest for some kind of application, either because their luminescence is so characteristic that it can be used for analysis, or because it is so strong that it can serve for illumination or similar purposes.

2. Organic Compounds

A good many hypotheses have been enunciated in the course of a century concerning the connection between the chemical constitution and the fluorescence of organic compounds. Our knowledge, however, of such relations is still very meager and can be reduced to two or three sentences.

The problem is too frequently confounded with the problem of *light absorption* in organic compounds. This second problem has been resolved semi-empirically to a certain degree by the dyestuff chemistry. For the simplest cases it is even accessible to exact treatment by quantum mechanics.[11a] Apart from the fact that light absorption is essential for the production of photoluminescence, and that, by Stokes' law, the wavelengths of the absorption bands and the emission bands are related to each other, the fluorescence problem has nothing to do with the absorption problem. A perfect knowledge of the light absorption power of a molecule does not provide the clue to the puzzle whether the molecule is able to re-emit absorbed energy as light or whether the molecule converts it into heat or another form of energy, or in other words: why and under what conditions an organic compound is or is not photoluminescent.

In principle the different behavior of different molecules can be ex-

* The latest compilation of this kind seems to be the one in Kayser's *Handbuch der Spectroscopie*, Vol. 4. This list was very complete in its time (1908), but since then the material has increased at least tenfold.

[11a] A. L. Sklar, *J. Phys. Chem.*, **5**, 669 (1937).

plained from the theoretical point of view. If light energy is absorbed by a molecule and is neither re-emitted in the form of luminescence nor spent in some kind of chemical reaction, it can only be converted into heat. However, according to the Franck-Condon principle, a direct transition of electronic excitation energy into kinetic energy of the surrounding molecules (or into heat) has an exceedingly small probability. But if a polyatomic molecule in a state of electronic excitation and small vibrational energy can reach a nuclear configuration which can also be reached in the electronic ground state with high vibrational energy, then the passage from one of these states into the other can have a very great probability. Thus by a process of "internal conversion" the absorbed light energy is at first converted into oscillations of the atoms forming the absorbing molecule and from there it is transferred into translation energy of other molecules.[11b] If the probability of internal conversion is much greater than the probability of light emission, the molecule is not able to fluoresce. Actually no rule is known which would allow the prediction of the probability of internal conversion in a given molecule, and the problem of the appearance or non-appearance of fluorescence is not yet much advanced by these theoretical considerations.

It is certain that a closed ring structure favors the appearance of luminescence by the rigidity which it confers upon the molecule.[12] Practically all aromatic hydrocarbons consisting exclusively of condensed phenyl rings are fluorescent, from benzene up to anthrodianthrene containing nine such rings. The same is true for many heterocyclic closed ring compounds like coumarin, acridine, carbazole, quinine and many others. Diphenyl, in which two benzene rings are linked by a simple bond, is much less fluorescent than carbazole or phenanthrene.[13]* But to make this rule not too general, the diphenyl polyenes show a very strong U.V. or visible fluorescence.[14]

It is, moreover, a rule that the substitution of hydrogen atoms in the phenyl rings of an aromatic compound by certain other atoms or groups, especially by halogens, reduces their fluorescence, even though their absorption power is increased. This is, for instance, true for chlorobenzene as compared to benzene, or for erythrosin as compared to fluorescein. Many other substitutions are mentioned in older treatises as "auxoflor" or "diminiflor,"[15] but these statements are very conflicting, they refer in

* Compare the formulae in Tables XVII and XVIII.

[11b] J. Franck and R. Livingston, *J. Chem. Phys.*, **9**, 184 (1941).

[12] J. Stark and R. Meyer, *Physik. Z.*, **8**, 250 (1907).

[13] H. Ley and H. Specker, *Z. wiss. Phot.*, **38**, 96 (1939).

[14] K. W. Hausser, R. Kuhn and E. Kuhn, *Z. physik. Chem.*, **B29**, 417 (1935).

[15] H. Kaufmann, *Physikalische Eigenschaften und chemische Konstitution.* Enke, Stuttgart 1920.

general only to a very restricted type of compounds and they do not take into account simultaneous changes of the absorption power. To mention just one example, the fluorescence spectra of xylene, toluene, and other simply substituted benzene derivatives very closely resemble the spectrum of benzene itself, but naphthylamine shows a strong blue-green fluorescence, while the emission spectrum of naphthalene is limited to the ultraviolet region between 3000 and 3700 Å.

None of the rules found so far is able to explain why the fluorescence yield differs so widely under similar conditions and why it is influenced so differently by the same external conditions. For instance, while under black light excitation the fluorescence yield for anthracene dissolved in benzene is 24%, it is close to 100% for pure crystalline anthracene. Naphthacene, hardly fluorescent as a pure crystal and yielding not more than 6% in xylene solution, has a fluorescence efficiency of nearly 100% when dissolved in solid anthracene. And rubrene, with almost no fluorescence in the pure solid state, can be excited to most brilliant fluorescence with a quantum yield close to 100%, when dissolved in benzene.[16]

Of more than 1,450 dyestuffs listed in the color index not more than 85 are characterized as fluorescent. Of these not a single one belongs to the most extensive group of the azo dyestuffs. The most brilliantly fluorescent compounds are to be found in the xanthene group: fluorescein, eosin and the rhodamines; in the acridine group: euchrysine, trypaflavine, choriphosphine; in the thiazole group: primulin and thioflavin; in the azine group: magdala red and safranine; and amongst indanthrene dyes, which are ketones of high aromatic hydrocarbons.

Comparing these dyestuffs with others, it is remarkable that they once more consist almost exclusively of perfectly closed rings.[12] It fits well into the rule, that diphenyl and triphenyl dyes like auramine, malachite green, or crystal violet are not fluorescent in alcoholic or aqueous solutions as are all the others mentioned above. They are closely related to the xanthene or acridine dyestuffs, but have an open bridge between two phenyl rings which is closed into a ring in the fluorescent compounds.

It must be emphasized that the fact that a dye is not characterized as fluorescent in the color index is no proof that it is not fluorescent at all. In some cases, as for erythrosin and rose bengale, which are expressly singled out as not fluorescent, the fluorescence yield is very small indeed in alcoholic or aqueous solutions at room temperature (Table IV). In other cases like thionine and methylene blue the red fluorescence has probably been overlooked, because it is best excited by light of nearly the same wave-length.

Apart from these rather unimportant exceptions, however, the character-

[16] J. W. Bowen and A. H. Williams, *Trans. Faraday Soc.*, **35**, 765 (1939).

should not be used with much confidence.* The only exception is quinine and its salts, which have been examined very carefully and under very different experimental conditions.

The exact spectral location of the absorption and luminescence bands of organic compounds is influenced by the nature of the solvent or adsorbent within certain limits. This influence does not always act in the same degree or even in the same direction for different compounds, and there is no unequivocal connection with any property of the solvent, *e.g.*, its refractive index, its dielectric constant, or its dipole moment.† The same is true with respect to the fluorescence yield. If a compound has essentially the same luminescence spectrum as vapor, in liquid and solid solutions, and as pure solid, the fluorescence bands are always shifted in this order towards the red end of the spectrum.

Among the liquid solvents hexane is frequently the most useful. It has neither absorption nor fluorescence bands of its own in the spectral region above 2000 Å, it is chemically inactive, and it has no dipole moment. For the same reasons sugar is an advantageous solid solvent. The phosphorescence of most compounds is brighter in boric acid, but the emission spectra are influenced by the acidity of the solvent.[23] Finally it may be mentioned that most dyestuffs show new emission bands in solid solutions at low temperatures. These, however, will hardly be of any practical interest.

3. Pure Inorganic Compounds

If the number of pure inorganic substances is restricted to those which possess fluorescence power as a characteristic property of their molecules, the list is very short. In the first place it contains the rare earth metals

* According to Andant the fluorescence spectra of all solid alkaloids vary when the wave-length of the exciting light is changed. This is in contradiction to the behavior of almost all other fluorescent substances and seems to prove that the alkaloids under investigation were not pure.[21]

† This is apparently due to the fact that the superimposed influences of polarity (molecular electric moment) and index of refraction (dielectric constant for high frequencies) can act either in the same or in opposite directions. According to results published by Sheppard the absorption bands of a great many dyestuffs are shifted quite regularly towards greater wave-lengths with decreasing index of refraction of the solvents as long as only solvents of the same polarity are taken into account. The same may be true for the fluorescence bands, though here no actual measurements are at hand.[22]

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[21] P. Andant, *Compt. rend.*, **185**, 713 (1927). Also P. W. Danckwortt, *Lumineszenz-Analyse*, Akademische Verlagsgesellschaft, Leipzig 1928 (3rd ed., 1934); and J. A. De Ment, *Fluorescent Chemicals*, Chemical Publ. Co., Brooklyn 1942.

[22] E. Sheppard, *Rev. Modern Phys.*, **14**, 303 (1942).

[23] G. N. Lewis, D. Lipkins, and Th. T. Magel, *J. Am. Chem. Soc.*, **63**, 3005 (1941).

europium, dysprosium, therbium, samarium, and gadolinium or rather their trivalent positive ions Eu^{+++}, Dy^{+++}, Tb^{+++}, Sm^{+++} and Gd^{+++},[24*] and the uranyl salts or, rather again, the uranyl ion UO^{++}.[25] Then follow somewhat less decidedly the platinum cyanide radical and finally the siloxene group $Si_6H_6O_3$, and this is about all.

The absorption and fluorescence spectra of the rare earth ions are exceedingly characteristic (Fig. 40). With comparatively small shifts they remain the same in all kinds of liquid and solid solutions and in a great number of organic and inorganic salts. The anion in the solid salts and the solvent in the solutions have only a secondary influence. In a few solid

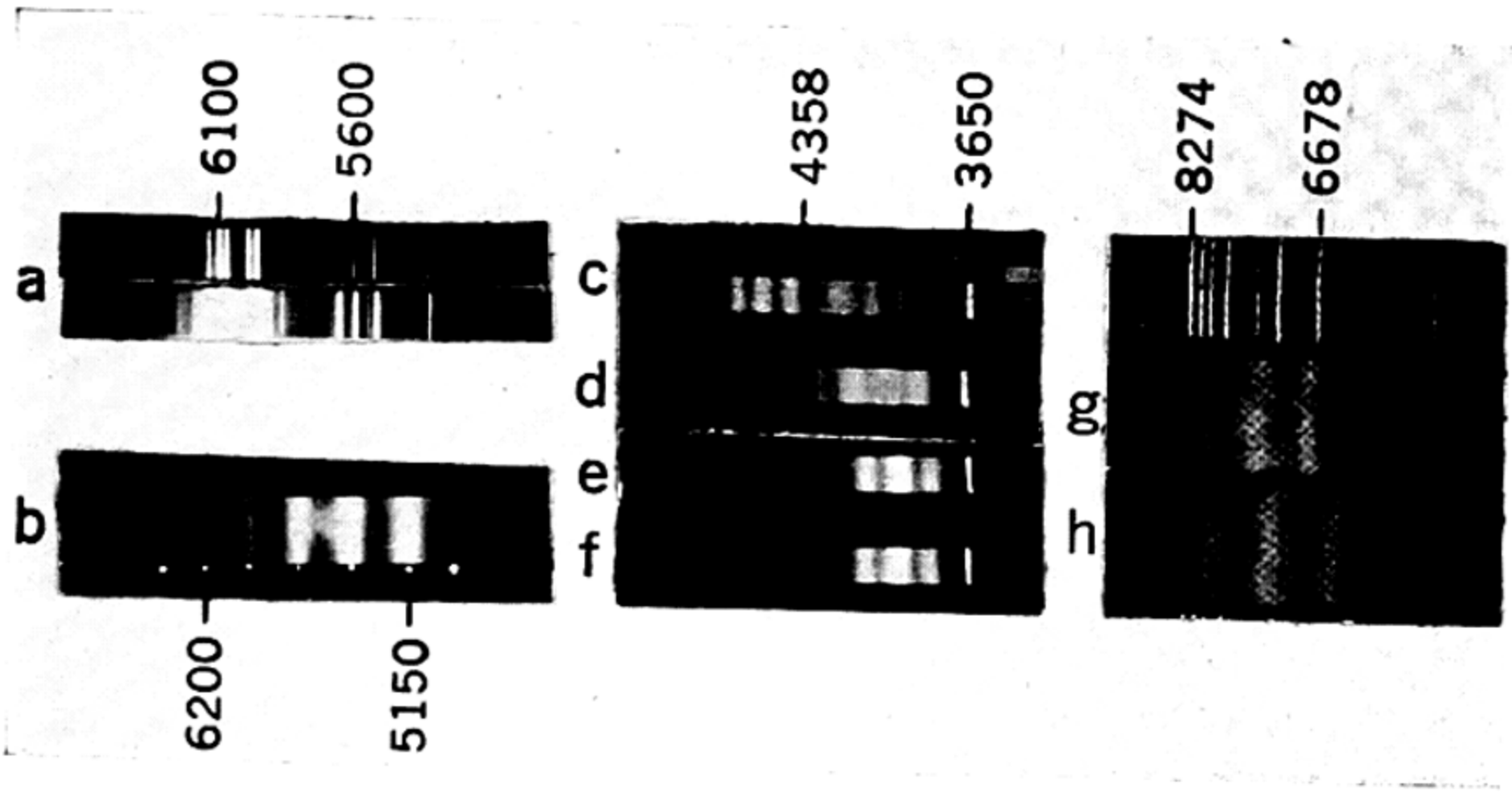

Fig. 40.—Characteristic fluorescence spectra.

a: Europium salt.
b: Uranyl sulfate in water.
c: Anthracene commercial, solid.
d: Anthracene pure, solid.
e: Anthracene commercial } dissolved
f: Anthracene pure } in benzene
g: Chlorophyll a
h: Chlorophyll b

crystals as in the anhydrous chlorides and the oxides the fluorescence is missing.

The only metallic ion outside of the rare earth group known to be

* Other rare earth ions like those of prascodymium or erbium are good activators as impurities in other crystals or glasses, but they are not fluorescent as pure salts or in liquid solutions. It should be mentioned, however, that some divalent rare earth ions also are fluorescent in aqueous solution. Their spectra are different from those of the trivalent ions and much less characteristic.

[24] R. Tomaschek and O. Deutschbein, *Ann. Physik*, **16**, 943 (1933); **28**, 673 (1937); **29**, 311 (1937).

[25] E. L. Nichols and H. L. Howes, *Carnegie Inst. Wash. Pub.*, No. 298 (1920).

fluorescent in aqueous solution is the thallous ion Tl^+.[26] The luminescence, excited only by short wave-length ultraviolet radiation ($\lambda < 2500$ Å), is much enhanced in solutions containing high concentrations of Cl^- or Br^- ions, apparently due to the formation of some complex ions. Even in pure water the solvation of the Tl^+ ion plays a part in the fluorescence. Pure thallous salts in the crystalline state are not fluorescent.

While the fluorescence spectra of the rare earth ions are typical atomic line spectra, those of the UO^{++} ions are typical molecular band spectra (Fig. 40). They are observed in almost all solid uranyl salts (sulfate, chloride, phosphate, acetate, and also many double salts such as sodium uranyl sulfate) and their liquid and solid solutions. Also in this case the nature of the anion, the second metal in a double salt or the solvent does not change the general aspect of the emission spectrum. It must be emphasized that the fluorescence of uranyl salts under light or cathode ray excitation has no connection whatever with their radioactivity, notwithstanding the fact that by an erroneous analogy the fluorescence of uranium salts led Becquerel to the discovery of radioactivity.

The luminescence of the rare earth ions, as well as of the uranyl ion, is a "slow fluorescence" with a relatively long lifetime of the order of 10^{-2} and 10^{-4} sec. respectively.[27] The fluorescence spectra correspond to forbidden transitions (electric quadrupole or magnetic dipole radiation) in both cases. Notwithstanding the long lifetime of the excited states the rare earth fluorescence is very slightly sensitive to quenching, the fluorescence yield being very high in all kinds of liquid solutions. On the other hand the uranyl fluorescence is easily quenched in liquid solutions by most organic compounds and the yield is low in aqueous solutions.

The platinocyanides were quoted above as less characteristic for this class, because until recently their very strong fluorescence seemed to be restricted to the crystalline state and, for color and intensity, highly dependent on the second metal, on the crystal water content and on the symmetry class of the crystal lattice. Khvostikov proved, however, that the $Pt(CN)^{--}$ ion is itself fluorescent, although its fluorescent power is greatly enhanced by the formation of complex molecules in the crystals.[28]

The fluorescence of siloxane has been observed only in solid compounds, but considering its ring structure, which is very similar to the structure of the benzene ring, it seems justified to assign the fluorescence to the molecule itself and not to an impurity. Besides, this fluorescence has so far no importance for any kind of application.[29]

[26] P. Pringsheim and H. Vogels, *Physica*, **7**, 225 (1939).
[27] F. Perrin and A. Delorme, *J. phys. radium*, **10**, 177 (1925).
[28] J. A. Khvostikov, *Physik Z. Sowjetunion*, **9**, 210 (1936).
[29] H. Kautsky and O. Neitzke, *Z. Physik*, **31**, 60 (1925).

There are several simple inorganic compounds which can be excited to strong fluorescence in the crystalline state only, apparently without containing any "activating" impurity.[30] The most important and most thoroughly investigated of these compounds is zinc sulfide. It is generally admitted now that in fluorescent ZnS "interstitial" zinc atoms play the part of an activating impurity. With regard to many other salts listed by different authors as being fluorescent it is very probable that the samples under investigation were not sufficiently pure. Frequently even the fluorescence color is not the same for the same compound according to the assertions of different authors. Calomel probably belongs to the type of crystals without foreign impurities. Under black light excitation it always emits a strong orange fluorescence. However, it is practically impossible to prepare mercurous chloride (Hg_2Cl_2) which does not contain some mercuric chloride and some free mercury in equilibrium.

The Mn halides, Mn silicates and perhaps some other manganese salts are fluorescent in the crystalline state under black light excitation.[31] The emission spectra are so characteristic that one is forced to ascribe them to a complex containing the Mn^{++} ion, and not to some foreign impurity. Mn is also one of the most effective activators for other crystals as shown in Table IX (see p. 83), and thus it seems reasonable to suppose that activating interstitial Mn ions are the origin of the luminescence in both cases. In aqueous solutions of Mn^{++} salts, manganates, or permanganates, no luminescence due to the presence of manganese has ever been observed.

It is much more questionable whether the fluorescence of another group of inorganic crystals should be ascribed to the existence of "interstitial" metal atoms. The most important member of this group is $CaWO_4$. It is quite plausible that the complex ion WO_4^{--} is the carrier of the fluorescence power in calcium tungstate just as the UO_2^{++} ion is the "fluorophor" in the uranyl salts. Fluorescence of isolated WO_4^{--} ions has never been ascertained. However, since "pure" crystalline ZnS, CdS, $CaWO_4$, etc., can also be activated by foreign impurities, and since they have in their general behavior as well as in the mode of their applications almost everything in common with the typical "impurity" phosphors, they are treated jointly with these in the following section.

4. Synthetic Inorganic Phosphors

Almost every crystalline inorganic salt which is not strongly colored and contains some sort of impurity is more or less luminescent, but a relatively small number of such compounds has been found to be serviceable for practical application. The properties wanted are not the same for every

[30] F. Seitz, *J. Phys. Chem.*, **6**, 454 (1938); N. Riehl, *Ann. Physik*, **29**, 630 (1937).
[31] J. T. Randall, *Proc. Roy. Soc. London*, **A170**, 272 (1939).

purpose, but in general the following conditions must be fulfilled: high luminous yield, sometimes in a specific color; if destined for photoluminescence, excitation by light of certain wave-lengths; stability against destruction by exciting radiation as well as against moisture and atmospheric influence; high melting point; high upper temperature limit of luminosity; long afterglow in some cases, no afterglow in others.

Table VIII contains the basic materials for all important phosphors which are in general use. Selenide and oxide phosphors[32] and vanadates[33] with properties similar to those of the sulfides and tungstates, respectively, have been prepared but have not yet found practical application. While papers dealing with alkaline earth and zinc sulfide phosphors are almost innumerable, and fairly complete accounts on silicate and tungstate phosphors are at hand, publications concerning borate or phosphate phosphors are hardly existent.

ZnS and CdS and the tungstates and molybdates belong to the class which is fluorescent without a foreign activator. They are phosphorescent, however, exactly like all the others only when activated by some impurity.* In the latter case the blue fluorescence of ZnS is suppressed by the emission bands of the activator (Ag, Cu, Mn).[35] The luminescence of $CaWO_4$ does not vary with regard to its color when the material is activated with As, Sb or Pb.[36] When activated with traces of Sm, $CaWO_4$ and $MgWO_4$ show a strong red afterglow of very short duration.[37] Pure Zn_2SiO_4 is not fluorescent under light excitation. Under electron bombardment it emits a pale blue fluorescence which vanishes as soon as the phosphor is activated with Mn.[33] The afterglow of manganese activated zinc silicate decays exponentially with a half life of about 10 milliseconds. After about 30 milliseconds a second phase of the afterglow with a much slower hyperbolic decay prevails, contributing only a few per cent to the total light emission. By addition of 0.5% arsenic oxide to the phosphor the relative contribution of the second emission phase increases to 75% of the total output, while the initial intensity decreases only by about 15%. Thus the average duration of the afterglow becomes appreciably longer, the luminescence spectrum remaining unaltered. With higher arsenic concentrations (5%)

* Below −100° C. "pure" $CaWO_4$ shows a long lasting afterglow according to Tiede and Schleede.[34]

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[32] G. R. Fonda, *J. Phys. Chem.*, **44**, 435 (1940).
[33] H. W. Leverenz and F. Seitz, *J. Applied Phys.*, **10**, 479 (1939).
[34] E. Tiede and A. Schleede, *Z. Elektrochem.*, **29**, 305 (1923).
[35] J. H. Gisolf and F. A. Kroeger, *Physica*, **6**, 1101 (1939).
[36] F. E. Swindells, *J. Optical Soc. Am.*, **23**, 129 (1933).
[37] R. P. Johnson and W. L. Davis, *ibid.*, **29**, 283 (1939); W. De Groot, *Physica*, **7**, 432 (1940).

the luminescence is completely quenched. Similar effects are observed with cadmium silicates and zinc beryllium silicates.[38]

Of the phosphors listed in Table VIII the sulfides alone (and also the selenides and some oxides) can be prepared so that they yield a persistent phosphorescence, sometimes lasting over many hours at room temperature. A relatively strong afterglow of the longest duration is obtained with some CaS and SrS phosphors. The afterglow of Cu activated ZnS immediately after excitation is exceedingly brilliant, but fades much faster than the luminescence of the Ca and Sr phosphors.[39] The phosphorescence of Ag activated ZnS is only of short duration.[40]

The luminescence processes of short duration, which are in general the most important ones for fluorescent lamps and fluorescent screens, belong in part to the hyperbolic (bimolecular) type as for ZnS or CdS, and in part to the exponential type as for the silicate phosphors or $CaWO_4$.[41] As the

TABLE VIII

BASIC MATERIALS OF PHOSPHORS

Sulfides of Zn, Cd, Ca, Sr (Mg)*
Tungstates of Ca, Cd, Mg (Li)
Molybdates of Ca (Mg)
Silicates (germanates) of Zn, Be, Cd (Zr, Ti, Mg)
Borates of Zn, Cd
Phosphate of Cd

* Parentheses (. .) indicate that the phosphors prepared with that metal are less important.

total duration of the afterglow is in general only of the order of milliseconds, this discrimination is interesting only from the theoretical viewpoint.

Only the crystalline modifications of the compounds listed in Table VIII are luminescent. Tungstates or sulfides precipitated as amorphous powders* or silicate gels are not fluorescent.[42]† The crystallization is ob-

* It is very instructive in this connection that KCl precipitated from an aqueous solution containing traces of a thallous salt shows not only fluorescence, but even a long lasting phosphorescence, after being superficially dried. For various reasons these phosphors are useless for practical applications.

† According to Fonda a red fluorescent modification of Mn activated zinc silicate is amorphous. The fluorescence is rather weak and the question concerning the noncrystalline structure seems to be not quite settled.

[38] H. C. Froelich and G. R. Fonda, *J. Phys. Chem.*, **46**, 878 (1941).

[39] G. F. A. Stutz, *J. Optical Soc. Am.*, **32**, 626 (1942).

[40] A. Schleede and B. Bartels, *Z. tech. Physik*, **19**, 365 (1938).

[41] R. P. Johnson, *J. Optical Soc. Am.*, **29**, 283 and 387 (1939); N. C. Beese, *ibid.*, **29**, 26 (1939); W. De Groot, *Physica*, **6**, 275 (1939).

[42] E. Tiede and A. Schleede, *Z. Electrochem.*, **29**, 305 (1923).

tained by firing the precipitates at temperatures which are different for different compounds. Simultaneously the atoms of the activating impurities are enabled to diffuse into the crystal lattice of the basic material. The process of crystallization and of formation of the phosphor is greatly facilitated by the presence of a flux, some colorless inorganic salt like KCl, $CdCl_2$, LiF, Na_2SO_4, etc. The part played by the nature of the flux is not too well understood. It does not seem to have a direct influence on the finished phosphor. Frequently it is possible to remove the flux after the preparation by means of a solvent which does not attack the phosphor itself, without any change of its luminescent properties.[43] Some of the phosphors can also be prepared, at higher firing temperatures, without the use of a flux. Probably the action of the flux is of a secondary nature. It determines the temperature at which crystallization sets in, the speed of crystallization, and the diffusion of the activating impurity, and thereby the quality of the finished phosphor. The choice of the flux which is most advantageous for the preparation of a phosphor with special properties is still more or less a matter of empiricism, as pointed out in the historical introduction. When fluorides are used as flux, the resulting phosphors are very hard and difficult to grind. Partial vitrification of the final product in the oven should always be avoided for the same reason. Small laboratory samples are produced easily, but when batches of 25 pounds and more are fired at a time, the oven heat distribution throughout the powder is a difficult problem.

The question of the importance of grinding and of particle size for the properties of phosphors is still somewhat controversial. According to Lenard the grinding itself destroys the luminosity of the sulfide phosphors ("Druckzerstoerung"). Other authors are of the opinion that the surface layers of the crystalline grains differ in structure from the deeper layers which are prevalent in larger grains. Riehl and Ortmann assert that the real luminous yield is changed very little by grinding, and that the apparent decrease of luminosity is due to the stronger diffuse reflection of exciting light by too finely ground powders.[44] At any rate it does not seem to be advisable to grind sulfide phosphors into particles of diameters less than 0.1 mm. In contradistinction the fluorescence brightness of silicate phosphors is supposed to increase with decreasing particle diameters down to 0.0008 mm.[45]

The number of impurity molecules able to activate phosphors is very large; it seems to be largest in the case of the alkaline earth sulfide phos-

[43] E. Tiede and A. Schleede, *Chem. Ber.*, **53**, 1721 (1920); G. R. Fonda, *J. Phys. Chem.*, **44**, 851 (1940).

[44] N. Riehl and H. Ortmann, *Ann. Physik*, **29**, 556 (1937).

[45] M. S. Oldham and W. Kunerth, *J. Optical Soc. Am.*, **31**, 102 (1941).

phors. The same activators need not be serviceable in general for different basic materials. One condition seems to be that the ionic (or atomic?) radius of the activator is smaller than the radius of the cation of the basic lattice.[46] Table IX gives a survey of the more important activators for different phosphors. If an element listed in the top line is marked + it is an activator for the phosphor in question; if marked −, it does not activate; if marked *q* it is a "quencher." A question mark means that nothing has been published about the case.

It is certain that the activating impurities do not occupy analogous positions in the lattices of all phosphors and that they do not have identical functions in different cases, even in the same basic material. In zinc sulfide Cu and Ag go into interstitial positions. By heating a "pure" ZnS phos-

TABLE IX

ACTIVATORS FOR DIFFERENT PHOSPHORS

Phosphor	Activating impurity										
	Cu	Ag	Bi	Mn	Pb	Sn	As	Sb	Sm*	Fe	Ni
CaS	+	+	+	+	+	+	−	+	+	+	+
SrS	+	+	+	+	+	+	−	?	+	−	+
MgS	−	−	+	+	?	?	−	+	+	?	?
ZnS	+	+	−	+	−	−	−	−	?	q	q
CdS	+	+	−	+	−	−	−	−	?	q	q
$CaWO_4$	−	−	−	q	+	−	+	+	+	(q)	(q)
Zn_2SiO_4**	q	−	?	+	−	−	−	−	?	q	q
ZnB_2O_4	?	?	+	+	?	?	?	?	?	?	?
CdB_2O_4	q	?	+	+	?	?	?	?	+	q	q
$Cd_3Zn_3(PO_4)_2$	?	?	?	+	?	?	?	?	?	?	?

* And other rare earths.

** The same for other silicates and germanates.

phor in contact with Cu_2S or Ag_2S, Cu or Ag respectively migrates into the ZnS lattice at temperatures between 300 and 400° C. at which no exchange between the Zn ions and the ions of the foreign metal can occur. After some time the fluorescence of the pure zinc sulfide is supplanted by the luminescence due to the activator. In contradistinction, Mn, another very efficient activator for ZnS, does not enter the lattice at temperatures below 950° C., but then real mixed crystals of (ZnMn)S are formed, with increased lattice dimensions, as shown by x-ray diagrams. And while the maximum concentrations at which Cu and Ag can be incorporated in ZnS are 10^{-4} and 10^{-6}, respectively, for the production of bright luminescent phosphors, as much as 50% MnS can enter the ZnS lattice.[46] The optimum

[46] N. Riehl and H. Ortmann, *Z. physik. Chem.*, **A188**, 169 (1941).

fluorescence yield corresponds to a concentration of 2.5% Mn but at much higher concentrations the fluorescence is still fairly bright.[47] It is of course not possible to decide whether the real carriers of the luminescence are not Mn atoms situated at points where the crystal lattice has some sort of a defect.

Like MnS, CdS forms mixed crystals with ZnS.[48] However, Cd does not act as an activating impurity: it modifies the fundamental lattice only, as shown by x-ray analysis, and simultaneously the long-wave limit of the fundamental absorption band of the mixed crystal is shifted toward greater wave-lengths. If such mixed crystals are activated with Ag or Cu the luminescence bands and the corresponding excitation bands are steadily displaced towards the red end of the spectrum with increasing Cd content, as shown in Table X and Fig. 41.[49] Thus it is possible to prepare ZnCdS (Cu) or (Ag) phosphors with varying luminescence colors from blue green to red and, by mixing these phosphors, to produce light of almost any de-

TABLE X

ABSORPTION AND LUMINESCENCE BANDS OF ZnCdS PHOSPHORS

% Cd		0	10	20	30	40	50	60	70	80	90	100
Long-wave limit of fundamental absorption		3460	3580	3720	3900	4115	4270	4450	4700	4820	4930	5120
Peak of fluorescence band	Cu	5200	5600	6100	6300	6400	6500	6600	6800	7000	7000	
	Ag	4450	4650	4800		5100	5600	6000		6700		7000

sired hue (Fig. 10, p. 20). Here again Mn differs widely as an activator from Cu and Ag. The Mn emission bands remain unaltered when a part of Zn is replaced by Cd in the fundamental lattice. The selective absorption bands on the long wave-length end of the absorption spectrum in Figure 41, which are characteristic of manganese, remain unaltered also with increasing cadmium concentration in a ZnCdS(Mn) phosphor.

Hardly anything is known about the location of the activating atoms in the lattice of the alkaline earth phosphors, notwithstanding the enormous amount of work published about these phosphors since the days of the stone of Bologna.

Like zinc sulfide, zinc silicate is able to form mixed crystals with the silicates of Mn, Cd and of Be, Zr, Ti and further, with the germanates of the

[47] F. A. Kroeger, *Physica*, **7**, 369 (1939).

[48] J. H. Gisolf, *ibid.*, **6**, 84 (1939).

[49] A. A. Guntz, *Ann. chim. phys.*, **6**, 5 (1926); F. A. Kroeger, *Physica*, **6**, 783 (1939); K. Kamm, *Ann. Physik*, **30**, 333 (1937).

same metals. Of all these additions to the original silicate Mn is once more the only activator, as a matter of fact the only known activator for silicate phosphors. The other admixtures change the lattice dimensions and influence the location of the Mn fluorescence band. The optimum concentration of Mn is between 0.5 and 2.5 molar. Above 2.5% the luminescence intensity falls off rapidly at room temperature. At liquid air temperature Zn_2SiO_4 phosphors with 50% Mn still show a bright luminescence (curve b in Fig. 42).

Mn activated Zn_2SiO_4 can be prepared with three different emission bands: green, orange yellow, and red. The green band is the most luminous and is most easily obtained. The appearance of one or another of the bands depends mainly on the firing temperature and cooling speed of the phosphor after its preparation. X-ray diagrams prove that the crystal structure is different in the three cases (Fig. 43).[50] The hypothesis that the

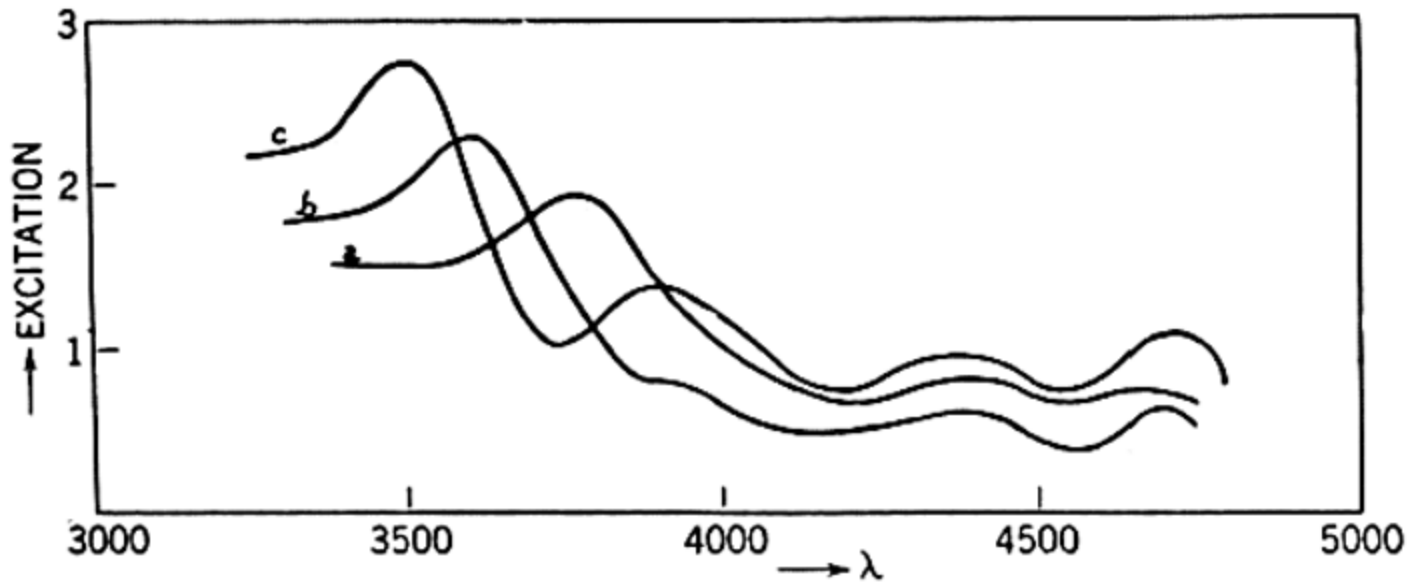

Fig. 41.—Excitation spectrum of zinc cadmium sulfide phosphors activated with manganese, with different cadmium concentrations (Kroeger).
a: 10% Cd. b: 5% Cd. c: 0% Cd.

three emission bands belong to different ionic states of the activating atoms cannot be accepted. Mn is incorporated in all zinc silicate phosphors as Mn^{++}.

In "mixed" ZnBe or ZnCd silicate phosphors, the yellow band prevails under all conditions of preparation. Probably the presence of Be or Cd favors the kind of crystallization corresponding to the emission of the yellow band. Preferential appearance of one band instead of another is not analogous to the steady shift of the fluorescence band in ZnCd sulfide phosphors with increasing cadmium concentration (Fig. 42, curves a and d).

The occurrence of more than one luminescence band in phosphors of apparently equal composition is by no means an isolated case. In all alkaline earth and zinc sulfide phosphors the same activating impurity is able to produce several "independent" phosphorescence bands. Which of these

[50] H. P. Rooksby and A. H. McKeag, *Trans. Faraday Soc.*, **37**, 308 (1941).

bands prevails in the luminescence spectrum depends in part on the momentary temperature of the phosphor and in part on the method of its preparation, the heat to which it has been fired, the duration of the firing, the nature of the flux, and also on the concentration of the activator. Dif-

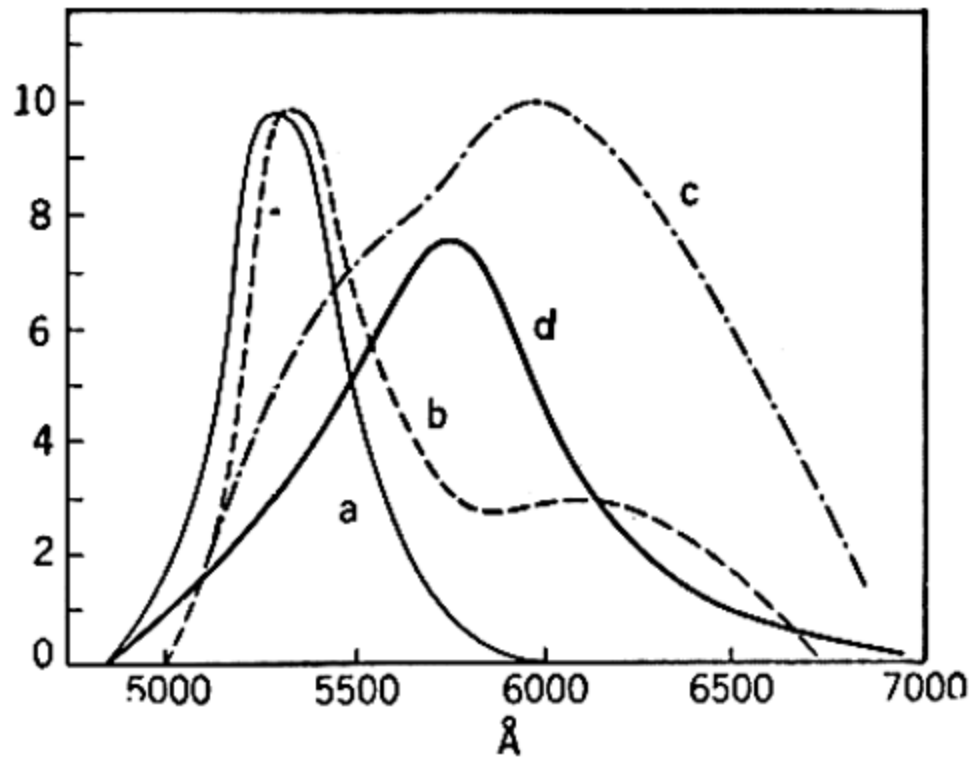

Fig. 42.—Emission bands of zinc silicate phosphors (Kroeger; Leverenz).
a: 5% Mn annealed (α-Willemite).
b: 20% Mn at −180° C.
c: 10% Be and 5% Mn at room temperature.
d: With 2% Mn quenched from 1600° C. to room temperature (β-Willemite).

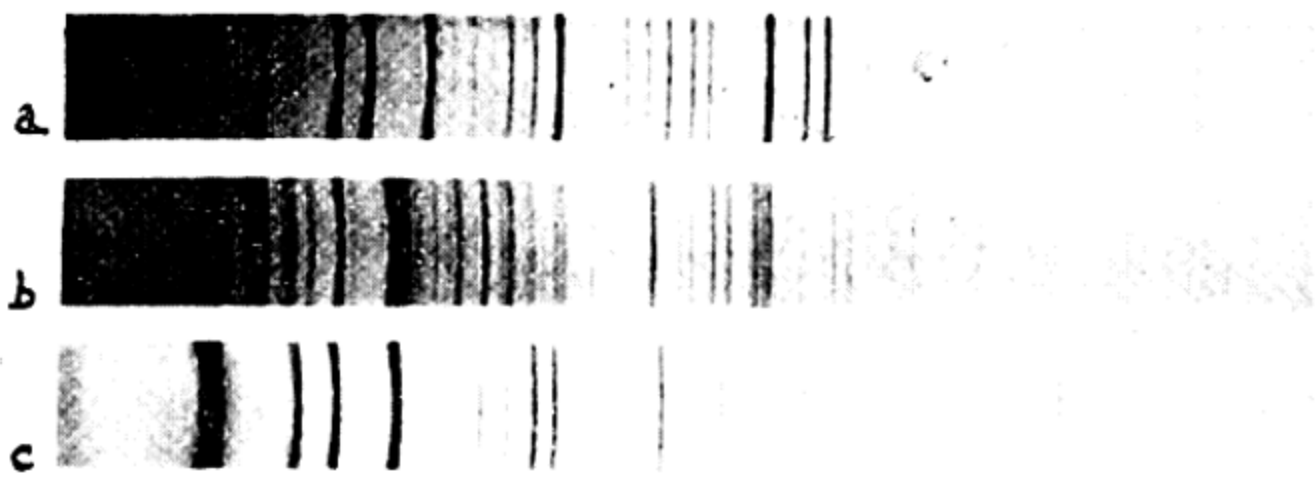

Fig. 43.—X-ray diagrams of zinc silicate phosphors (Rooksby and McKeag).
a: green fluorescent phosphor. b: yellow fluorescent phosphor.
c: non-luminescent cristoballite.

ferences in the crystalline structure play no part in the case of sulfide phosphors.* Not only the predominance of one of the independent bands, but

* ZnS is known to crystallize in two modifications, as regular sphalerite (blende) and hexagonal wurtzite, but there is hardly any difference between the luminescence properties of the two crystalline forms.

also the wave-length of the peak of each individual band is influenced by the conditions mentioned above.*

In the sulfide phosphors an increasing concentration of the activating atoms increases the intensity of fluorescence relatively to the intensity of phosphorescence. In order to obtain phosphors with a long lasting afterglow, the concentration of the activator must be kept low.† Under this condition the fluorescence is very weak, while the phosphorescence is at its best.[51] With regard to a so-called "optimum concentration," it is therefore essential to know whether the optimum for phosphorescence or for fluorescence is wanted. The value may also be different for excitation by light,

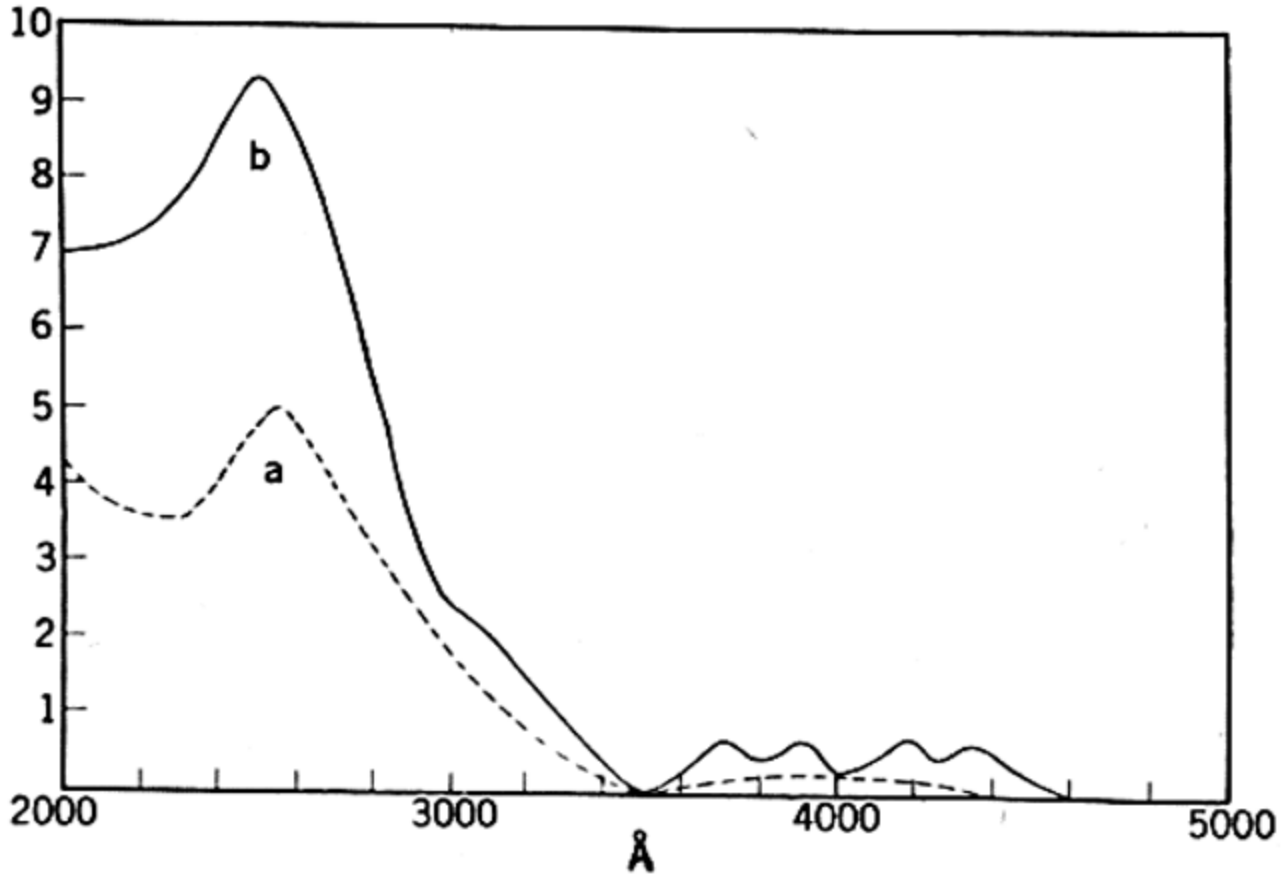

Fig. 44.—Excitation spectra of zinc silicate phosphors at different manganese concentrations (Kroeger). a: 1% Mn. b: 5% Mn.

cathode rays or x-rays. In the case of Zn_2SiO_4 (Mn) it even depends on the wave-length of the exciting light. For excitation by the line 3650 Å

* In order to complete this survey of the different ways by which the incorporation of an impurity may produce the activation of a crystal phosphor, the case of Al_2O_3 (corundum) may be mentioned, though aluminum oxide phosphors find hardly any practical application, apart from the use of synthetic rubies for jewelry. If the impurity, like Cr_2O_3, Fe_2O_3 or Ti_2O_3 crystallizes isomorphously with corundum, the impurity probably replaces the cations in the basic lattice without much strain, and the resultant crystal is only fluorescent. If the impurity crystallizes in a different symmetry class like MnO_2 or TiO_2, the crystal becomes phosphorescent.

† High temperature and long duration of firing is also advantageous for the production of phosphors with long persistent phosphorescence.

[51] P. Lenard, F. Schmidt and R. Tomaschek, *Phosphoreszenz und Fluoreszenz* (*Handbuch der Experimentalphysik, Vol. 23/1 and 2*), Akademische Verlagsgesellschaft, Leipzig 1928.

which is very slightly absorbed in the fundamental lattice (comp. Fig. 44) the optimum concentration is as high as 4%; for 2537 Å it is of the order of 2%;for 760 Å it is below 0.5%.[52a]

The optimum concentrations are very different for different activators in one basic material, but also for the same impurity in different materials. The fluorescence and phosphorescence of $CaWO_4$(Pb) is quenched if the Pb concentration exceeds 1%.[36] $LiWO_4$ containing as much as 20 and even 40% Pb is still strongly fluorescent and phosphorescent. Though pure calcium molybdate is luminescent itself, addition of $CaMoO_4$ to pure calcium tungstate destroys the fluorescence power of the latter.[52b]

In some cases the optimum concentrations are exceedingly small. Iron, for instance, can be used as activator in CaS at concentrations of the order of 10^{-6}. At higher concentrations it quenches not only its own luminescence, but also that due to any other activator present in the phosphor. Phosphorescence is always much more sensitive for quenching actions than fluorescence. According to Levy and West the addition of Ni at a concentration of 2×10^{-6} to a ZnS(Cu) phosphor destroys the phosphorescence excited by x-rays almost completely while the fluorescence is reduced to a much smaller degree and still remains at a very high level.[53] The addition of such "nickel killers" to zinc sulfide phosphors has made them useful for many applications where a strong afterglow would be harmful.

At higher concentrations of a quenching metal not only the phosphorescence but also the fluorescence is quenched. Even "activating" metals frequently become "quenchers" if their concentration is too high. Also in this case different phosphors react differently to the addition of the same impurity, as shown in Table XI.[54] Cu, the best activator for the sulfide phosphors, is a "killer" for silicates, borates and tungstates. Mn, a good activator for many sulfides and apparently the only one for silicates and borates, quenches the luminescence of tungstates. Cr acts similarly to, but less strongly than Ni and Fe, and is a good activator in very special cases only. Other heavy metals like Ag, Bi, Sn, Al in moderate concentration are relatively harmless in phosphors, which are not activated by these impurities. If a phosphor contains more than one activator, the corresponding emission bands are sometimes superimposed in the luminescence spectrum, as in the case of CaS activated with Mn and Bi. Or the emission band of one is suppressed by the emission band of the other, as for instance the Cu band by addition of Bi, or the Sm bands by the addition of Pr to a CaS phosphor.

For the different reasons mentioned in the foregoing sections all state-

[52a] A. Ruettenauer, *Z. tech. Physik*, **19**, 148 (1938).
[52b] A. Schleede and T. H. Tsao, *Chem. Ber.*, **62**, 763 (1929).
[53] L. Levy and D. W. West, *Trans. Faraday Soc.*, **35**, 128 (1939).
[54] J. W. Marden and G. Meister, *Trans. Illum. Eng. Soc.*, **34**, 503 (1939).

ments regarding color, intensity and duration of luminescence for a given phosphor have not more than qualitative significance. For instance, the data published by different authors on the luminescence spectra of ZnCdS-(Ag) or ZnBe silicate phosphors, some of which are reproduced in Table X and Figure 42, disagree rather widely in many details. The optimum concentration of Mn in the same kind of silicate phosphors is given by three different authors for the same exciting radiation (Hg 2537 Å) as 0.6, 1.5 and 2.5%.

TABLE XI

INTENSITY OF FLUORESCENCE OF PHOSPHORS IN THE PRESENCE OF A "QUENCHER" OF CONCENTRATION c%

(Intensity of Phosphor Without Quencher = 100)

Phosphor	Quencher				
	c	Fe	Ni	Cu	Mn
Zn_2SiO_4(Mn)	0.01%	78	78	88	+
	0.1%	30	16	23	+
$CdSiO_3$(Mn)	0.01%	77	90	50	+
	0.1%	15	70	0	+
CdB_2O_4(Mn)	0.01%	80	90	93	+
	0.1%	47	65	47	+
$CaWO_4$	0.01%	65	?	?	79
	0.1%	37	?	?	47
$MgWO_4$	0.01%	93	100	99	?
	0.1%	83	100	87	?
CaS(Cu)	0.01%	30	40	+	+

For research work on phosphors it is of the greatest importance that all material used is of the utmost purity. According to the analysis reproduced on the labels, so-called pure oxides of the metals most frequently employed in the preparation of phosphors (Zn, Cd, Ca, Mg, W, B and Si) contain from 0.005 to 0.02% of other metals, in part Fe. In many samples the real percentage of impurities is much larger. It is advisable to start with water soluble salts like $Zn(NO_3)_2$, $ZnSO_4$, $Sr(NO_3)_2$, ammonium tungstate, etc. The aqueous solutions are purified by electrolysis and repeated recrystallization. Then the intermediate compounds, carbonates, oxides, sulfides, tungstic acid, etc., are precipitated by the introduction of ammonium carbonate, H_2S, HCl, etc., into the aqueous solution and these are finally transformed into the phosphors.

For preparation on a commercial scale these precautions need not always

be taken. Especially in the case of CaS and SrS phosphors ordinary "pure" commercial oxides, hydroxides, or sulfides may give quite satisfactory results. But one must be prepared to obtain products of rather different quality every time a new batch of chemicals is taken into the mixture, even if these chemicals all come from the same source. And it may happen that the brilliant phosphorescence of a product is really due to an unknown impurity contained in one of the components of the mixture, so that it cannot be reproduced at will.

CaS and SrS phosphors are prepared by mixing the powdered oxides or hydroxides of the alkaline earth with an equivalent quantity of pure sulfur, 5 to 20% of a simple or compound flux and a very small quantity of the activating metal, which as a rule does not exceed 0.01%. Sr phosphors require only about half as much activating impurity as Ca phosphors. The mixed powder is fired during a period of about one hour to a temperature between 900 and 1100° C. and is then allowed to cool down slowly.

ZnS is much more sensitive to quenching or activating impurities than the alkaline earth sulfides; the quantity of activating metals is in the average only about 1/10 of the quantity used in CaS phosphors. Therefore the preparation of good ZnS phosphors is a more difficult task. For commercial production on a large scale as well as for laboratory research work the primary material must be very carefully purified. Even if zinc ore is provided in the form of ZnS, this ore must at first be converted into $ZnSO_4$ for a further treatment of the kind described above.* The firing of the sulfide, with or without an activator, is performed to great advantage in a high pressure furnace in the presence of a chemically inactive gas like nitrogen.[55a] The firing temperature must be of the order of 1200° C.

For the preparation of pure tungstate or molybdate phosphors, carbonates of Ca, Mg, etc. are heated with tungstic or molybdic acids for 30 min. to 1000° C. or 60 min. to 850° C. respectively, or the amorphous precipitates obtained from aqueous solutions of W or Mo salts are fired to about 1000° C. in the case of tungstates, but to not more than 850° C. in the case of molybdates. Special care must be taken to have the tungstates perfectly free from arsenate if phosphorescence of the product is to be avoided.

For the commercial production of fluorescent silicates and germanates and their combinations the different metals (Zn, Cd, Be, Zr, Ti, Ge) are precipitated from an aqueous solution together with Mn in the desired proportion upon finely divided silica (gel or quartz powder). This mixture is heated for an hour to temperatures between 1000 and 1500° C. Firing to high temperatures and rapid quenching to less than 1100° C. produces the

* According to a patent of the New Jersey Zinc Co. the zinc sulfate solution can be purified by boiling at first with crude ZnO and then with Zn dust.

[55a] E. Streck, *Z. physik. Chem.*, **A186** (1940).

yellow or red fluorescent types. The normal proportion of SiO_2 to ZnO is 2 moles to one. The resulting compound is always the orthosilicate, Zn_2SiO_4. A surplus of SiO_2 (3 or 4 moles instead of 2) favors the production of the yellow fluorescent silicate.

Only manganese activated phosphate phosphors are known. They are prepared by heating either pure cadmium phosphate ($Cd_3(PO_4)_2$) or a mixture of cadmium phosphate and zinc phosphate together with 1–2 per cent of manganese oxide to 700° C. for a period of 20 minutes.

In order to obtain fluorescent zinc borate, ZnO and H_3BO_3 in the molar proportion of about 57:43 are mixed with 1% of a Mn salt and heated to a temperature above 650° C. but not exceeding 950° C. While the mass fuses into a glass when quenched, it is converted into a strongly fluorescent microcrystalline powder by slow cooling. The fluorescence is green when the firing temperature is about 650°, and is red when the mass is fired to 950° C. In general both bands are superimposed producing a whitish luminescence. Without the addition of the activating manganese, "pure" zinc borate having undergone the same treatment is luminescent under cathode ray excitation. In this case the fluorescence and phosphorescence show a deep violet color, the emission band reaching from 4500 Å far into the U.V.

5. Minerals, Glasses

The number of fluorescent natural minerals is very large. With few exceptions they belong in the class of crystal phosphors activated by foreign impurities. The exceptions are uranyl compounds and Scheelite, the natural counterpart of synthetic calcium tungstate. In relatively few cases the activating impurity simultaneously produces the characteristic color of the mineral, which would go by another name without the coloring agent. Thus the red corundum only is called a ruby, only the green modification of spodumene is known as hiddenite. Much more frequently the impurity which is the carrier of the fluorescence is not an intrinsic component of the mineral. Calcites or fluorites or diamonds with red, green or blue fluorescence or no fluorescence are classified as calcites, fluorites and diamonds. They cannot be identified as such by observation of their fluorescence. Sometimes the nature of the activating impurity can be recognized by the analysis of the fluorescence spectrum. In by far the most numerous cases, however, the fluorescence is not only not characteristic of the mineral, but the impurity from which it originates is not even known. Such minerals find their place in a collection of fluorescent stones; they may be employed for some kind of decorative display but not for any really useful application.[55b]

[55b] C. B. Slawsa, *Cranbrook Inst. Sci. Bull.*, No. 5 (1935). Also H. C. Dake and J. A. De Ment, *Fluorescent Light and Its Applications*, Chemical Publ. Co., Brooklyn 1941; and J. A. De Ment, *Fluorescent Chemicals*, Chemical Publ. Co., Brooklyn 1942.

While the classification of fluorescent minerals as crystal phosphors activated by impurities is quite unequivocal, the problem is more complicated in the case of fluorescent glasses. The two best-known types of fluorescent glasses, canary glass and didymium glass, are easily dealt with because they contain uranyl or rare earth ions which are fluorescent in all kinds of solutions.* However, as already mentioned, nearly every silicate , phosphate or borateglass containing traces of a heavy metal is fluorescent when excited with ultraviolet light of short wave-length. According to Cohn[57] zinc borate glass activated with 2% Mn emits a strong orange fluorescence band with a peak at 6100 Å under the action of light of wave-lengths below 2500 Å. Kabakjian[58] asserts that the fluorescence is very weak as long as the borate is a glass and increases "tremendously" as soon as crystallization sets in. Curie[59] states also that the rather weak reddish fluorescence of many zinc borate glasses activated with manganese gives way to a strong green phosphorescence when the glass is devitrified or begins to crystallize. On the other hand Linwood and Weyl are of the opinion that the green luminescence of silicate glasses is due to Mn^{++} ions which have entered the network of the silicon dioxide, taking the place of Si^{++} ions, while they ascribe the red fluorescence to "interstitial" manganese ions.[60] Other glasses, especially colored glasses like some of the yellow Zeiss filters, can be excited to fluorescence by light of the near U.V. or even the blue-violet region of the spectrum. The question, whether germs of crystallization are always present in such glasses, is not quite settled.[61]

From the practical viewpoint the luminescence of glasses has for the present a rather negative interest insofar as the fluorescence of a container or a filter may mask another weak fluorescence under observation. It is not improbable, however, that within the near future fluorescent glasses will become important for the manufacture of fluorescent lamps. At any rate an increasing number of patents for the manufacture of fluorescent glasses has been filed lately in different countries.

* Didymium is a mixture of praseodymium and neodymium. While the pinkish color of didymium glass is due to selective light absorption by these two elements, the fluorescence is due only to Pr and to traces of Sm. Nd produces no visible fluorescence. Glasses activated with Eu, Tb, Tu, etc., are also fluorescent, but they are not manufactured on a commercial scale.[56]

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[56] O. Deutschbein, *Z. Physik*, **102**, 772 (1936).
[57] B. E. Cohn, *J. Am. Chem. Soc.*, **55**, 953 (1933).
[58] D. H. Kabakjian, *Phys. Rev.*, **51**, 365 (1937).
[59] M. Curie, *Trans. Faraday Soc.*, **35**, 114 (1939).
[60] S. H. Linwood and W. A. Weyl, *J. Optical Soc. Am.* **32**, 443 (1942).
[61] D. Dobischek, *Dissertation*, Berlin 1934; R. Tomaschek, *Trans. Faraday Soc.*, **35**, 148 (1939).

PART II

APPLICATION OF LUMINESCENCE

CHAPTER V

FLUORESCENCE ANALYSIS

1. Possible Fields for Analysis

Because of the minute quantities of some substances that can be traced by their fluorescence,* fluorescence analysis might seem to be one of the most promising fields for the practical application of luminescence. Several of the books mentioned in the bibliography on page ix deal almost exclusively with this aspect of the problem. Fluorescence analysis can be used for many different purposes; its potentialities, however, have probably been rather overestimated. It will never acquire an importance equal to that of the older spectrum analysis by means of flame, arc, or spark spectra, for two reasons which are more or less interdependent: fluorescence is in general not specific enough and it is too easily influenced by external conditions.

The lines of the spark spectrum of a metal have always exactly the same wave-lengths, which are measurable to within one-hundredth of an Ångstrom unit. By the appearance or nonappearance of a few such lines on a spectrogram, the presence or absence of the metal is proved beyond doubt. The same is true for the lines of the Raman spectrum of compound molecules with the only disadvantage that these spectra are relatively weak and therefore more difficult to obtain. Furthermore, both electric discharge spectra and Raman spectra are additive. The emission lines are not affected as to their wave-length nor in general as to their relative intensity by the presence of other metals or compounds. All constituents of any mixture can be identified by the superposition of their spectrum lines.

On the contrary, relatively few luminescence spectra of liquids or solids are so characteristic that they can be ascribed with certainty to a given carrier. The light emission by such a substance can be altered or totally suppressed by small amounts of another substance.† These facts do not have the same significance for every one of the various cases in which fluorescence analysis in the wider sense of the word can be employed, although they affect them all more or less. They are very detrimental in qualitative analysis, they are much less harmful in purity tests and cer-

* Fluorescein in water or anthracene in alcohol can be recognized by their fluorescence at dilutions below 10^{-10} grams per cubic cm.

† To a certain extent the existence of fluorescence is a more characteristic quality than the existence of light absorption in the same substance. However, the absorption spectra are much less subject to perturbations by impurities, and so even the analysis by means of absorption spectra has a much larger field of applicability than fluorescence analysis.

tain special cases of quantitative analysis, and their interference may be almost negligible in the discrimination between different natural or manufactured products or in the use of fluorescent *p*H indicators.

The main advantages of fluorescence analysis as compared with other types of spectrum analysis are the following: relatively unstable compounds can be tested which could not be subjected to an electric discharge or to heating in a flame, the intensities are much larger than in Raman spectra, much smaller quantities or concentrations are needed than for absorption spectroscopy, and the substances under investigation need not be transparent.

2. Qualitative Analysis in Inorganic Chemistry

The historical importance of the cathodoluminescence spectra in the discovery and separation of the rare earth metals has already been mentioned.[1] It should be added, though, that these achievements were somewhat retarded by the fact that certain spectra were ascribed to an element supposed to be pure or at any rate forming the bulk of a substance under observation, while they really belonged to a still unknown rare earth metal present as a small impurity.* For example it has been demonstrated quite recently that all visible fluorescence bands of didymium glass previously ascribed to the Nd content of the glass were due to a contamination of the Nd by traces of Sm.[2]†

However, since all their spectra have now been listed, the rare earth metals Sm, Eu, Gd, Tb, Dy, Pr, Nd, Er are easily identified by their photoluminescence or cathodoluminescence when they are dissolved in various colorless solids.‡ The salts of those rare earths which are photoluminescent in aqueous solutions can be traced in such solutions with the help of a small pocket spectroscope down to concentrations of 10^{-2} molar

* Even if a pure salt of a rare earth is luminescent, the fluorescence intensity is in general greater if the same substance is dissolved in another solid.

† The other visible fluorescence bands of didymium glass belong to Pr, the second component of didymium.

‡ Tomaschek has measured the fluorescence spectra of Sm in the following solid solvents: Oxides of Be, Mg, Ca, Sr, Ba, Zn, Ce, Th, Ga, Sc; sulfides of Mg, Ca, Sr, Ba, Zn; fluorides of Ca, Sr, Ba, Mg; and sulfates of Be, Ca, Sr, Ba, Na, K, Mg, Pb, Zn, Cd, Al, La, Gd. When obtained by precipitation from aqueous solutions the salts must always be heated to 600–800° C. in order to become strongly luminescent. The Sm spectra in the different solvents show essential differences but are all of the same type. The fluorescence lines of Nd are all in the infrared and those of Gd in the ultraviolet part of the spectrum. The other rare earth metals, La, Ce, Ho, and Lu, have no fluorescence line spectra in any kind of solution.[3]

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[1] W. Crooks, *Proc. Roy. Soc. London*, **28,** 477 (1849) to *ibid.*, **65** (1899); Lecoq de Boisbaudran, *Compt. rend.*, **100** (1885) to *ibid.*, **117** (1893).

[2] O. Deutschbein, *Z. Physik*, **102,** 772 (1936).

[3] R. Tomaschek, *Ann. Physik*, **16,** 930 (1933).

for Sm, 10^{-3} molar for Eu and Dy, and 10^{-4} molar for Tb.[4] By spectrophotographic methods much smaller quantities might be detected. Sm present in lanthanum oxide or gadolinium oxide at a ratio of 1:250,000 gives a fluorescence emission sufficiently strong for the identification of Sm. Very minute quantities of Sm, Eu, Dy and Gd are the source of the well-known and very characteristic line fluorescence of certain fluorspar varieties.[5]

By the action of x-rays or radium rays the trivalent ions of Sm, Eu, Yb and Tb dissolved in CaF_2, $CaSO_4$ or other salts are reduced to divalent ions, and these give rise to a new type of fluorescence spectra consisting of broader bands.[6] The red fluorescence of many fluorites and calcites and of apatites and zircons is due to Sm^{++}, while another red and a green emission band appearing only at low temperatures in the same crystals is due to Tb^{++} and Dy^{++}, respectively. Natural minerals showing this fluorescence probably were exposed to the weak radiation of some radioactive product over very long periods in the soil where they were found. If such crystals are heated to temperatures above 500° C. they frequently emit a strong thermoluminescence and their photoluminescence power is destroyed; it can, however, be regenerated by renewed radium irradiation.

Nearly all solids and, to a smaller degree, liquid solutions containing uranium in the form of UO_2^{++} ions, show the typical uranyl fluorescence. The details of the fluorescence bands, excited by violet light or cathode rays, vary with the components of the salt.[7] By an exact measurement of the wave-lengths of the individual bands in the fluorescence spectrum the nature of the uranyl salt under examination can be determined as uranyl sodium sulfate, uranyl nitrate, uranyl rubidium acetate, and so on. But a general survey of the five to seven brilliant green and yellow emission bands is sufficient to prove the presence of a uranium compound, as, for example, in minerals like sodalite, sapolite or hyalite.[8] In these cases the uranium content is not characteristic of the mineral as such, but is found only in certain samples. There are other minerals, like autunite, a uranyl calcium phosphate, or Schroeckingerite, a hydrated uranium calcium carbonate, in which uranium is an essential constituent and which can be excited to emit the uranyl fluorescence spectrum. Many other uranium minerals, amongst them pitchblende, are not fluorescent by themselves, but their uranium content can easily be converted into some fluorescent compound.

[4] H. Gobrecht and R. Tomaschek, *Ann. Physik.* **29,** 324 (1937).

[5] G. Urbain, *Ann. chim. phys.*, **18,** 365 (1909); W. J. Humphreys, *Astrophys. J.*, **20,** 266 (1904).

[6] K. Przibram, *Z. Physik*, **107,** 709 (1937).

[7] E. L. Nichols and H. L. Howes, *Carnegie Inst. Wash. Pub.*, No. 298 (1920).

[8] E. Iwase, *Sci. Papers Inst. Phys. Chem. Research Tokyo*, **37,** 58 (1940); H. Haberland *Wien. Ber. IIa*, **146,** (1937) and **147,** 137 (1938).

When by prolonged heating all rare earth fluorescence is destroyed in a fluorite crystal, a greenish fluorescence showing the well-known uranyl bands frequently survives.[9] In lithium fluoride, borax beads, phosphate beads, etc., 10^{-7} mole per cent of uranium can still be traced by the fluorescence test.[10] In the case of the rare earths the identification of the individual elements by means of the fluorescence spectra of their trivalent ions is much easier than by analysis of their highly complicated arc or spark spectra. The same applies to the fluorescence spectra of the uranyl compounds as compared with the arc and spark spectrum of uranium.

Chromium is another metal which under certain circumstances gives rise to very characteristic luminescence spectra.[11] Chromium is *fluorescent* only when it is incorporated in a crystal isomorphous with the Cr salt, *e.g.*, Cr_2O_3 in Al_2O_3 or $MgCr_2O_4$ in $MgAl_2O_4$. That the red color of natural ruby is produced by minute quantities of chromium dispersed in the corundum lattice was demonstrated by fluorescence analysis long before it could be proved by ordinary spectrum analysis, and even now no chemical test is sensitive enough to ascertain the presence of the metal in natural ruby.

A similar red fluorescence, although with somewhat different line spectra, is due to the presence of chromium in other gems. Emerald, alexandrite, and red spinel* are the most important ones. Accidental† Cr fluorescence can also be observed with individual samples of topaz, andalusite and usually rather weakly with sapphire, which owes its blue color and its orange fluorescence to Ti_2O_3 incorporated in the corundum lattice.

When Cr is dissolved in lithium fluoride or other salts which do not crystallize isomorphously with the corresponding chromium salt, other much less characteristic fluorescence spectra with intensity maxima in the green region are observed. Pure chromium salts or chromium alums are not fluorescent, though their absorption spectra show the same kind of line-like bands which are characteristic of the red fluorescent crystals.

All other metals, even if they are excellent activators for phosphors, can hardly be identified in a general way by means of their fluorescence spectra. One may be sure, of course, that a sample of zinc silicate with a strong green

* Natural Mg spinels and synthetic Zn spinels ($ZnAl_2O_4$) activated with Cr show the typical red Cr line fluorescence. In most samples of natural Zn spinels this fluorescence is quenched by an admixture of iron.

† It is called accidental because many samples of the same minerals contain no chromium. If the fluorescence of rubies from Ceylon is of a more yellowish color, these crystals must contain still another impurity, perhaps titanium or manganese.

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[9] H. Haberland, *Wien. Anz.*, **1935**, p. 273.

[10] E. Nichols and M. K. Slattery, *J. Optical Soc. Am.*, **12**, 499 (1926); M. K. Slattery, *ibid.*, **19**, 175 (1929).

[11] O. Deutschbein, *Ann. Physik*, **14**, 712 (1932); E. Tiede and H. Lueders, *Chem. Ber.*, **66**, 1681 (1933).

fluorescence contains Mn. But as mentioned in Chapter IV, even in Zn_2SiO_4 manganese may produce a fluorescence of a different color. The observation of a green or red fluorescence in a material of unknown composition is under no conditions a safe proof for the presence of manganese.* Similarly, metals like copper or bismuth may be recognized easily enough by their phosphorescent properties when they act as "phosphorogens" in a given alkaline earth sulfide or oxide phosphor. Lenard therefore recommends the tracing of small quantities of metals by incorporating them in such phosphors. The phosphorescence bands, however, are characteristic of a metal only in one well-defined phosphor and are quite different in some other phosphor†; thus the original material under investigation would have to be converted into the sulfide of a certain alkaline earth, and even then the characteristic phosphorescence of the metal might be masked or suppressed by the presence of another metal of even much smaller concentration.

Tanaka has published a number of papers in which he contends that the bands of the fluorescence spectra of impurity activated crystal pnosphors show series of equidistant intensity maxima.[12] The spacing of these maxima is supposed to be independent of the nature of the basic material and characteristic of the activating metal. His list covers all metals of the periodic system from lithium to bismuth. The frequency intervals $\Delta\nu$ decrease steadily from 122.5 cm.$^{-}$1 for Li to 78 cm.$^{-1}$ for Bi.** The existence of such regular and characteristic frequency intervals in the fluorescence spectra would be exceedingly advantageous for fluorescence analysis. The improbability of the validity of Tanaka's result has already been discussed elsewhere from a theoretical viewpoint.‡ A merely theoretical

* For instance the green or reddish fluorescence of hiddenite or Kunzite, varieties of spodumene from California, is usually ascribed to the presence of Mn. This, however, must remain not much more than a guess as long as it cannot be ascertained by another method.

† Compare for instance the emission bands of the different ZnCdS phosphors activated with copper (see Table X).

** A curve showing the values of $\Delta\nu$ as a function of the atomic weights is to be found in books *A* 5 and *B* 11 in the bibliography on pages ix and x.

‡ The idea that such regularly spaced series of maxima should exist, originated apparently from the well established aspect of the uranyl fluorescence bands. In this case the band structure is due to the superposition of an electronic transition and the nuclear vibrations within the UO_2^{++} ion. If similar band spectra should be produced by a metal like copper or thallium imbedded in some basic crystal like calcium sulfide of strontium oxide the vibrational frequency intervals would certainly be characteristic for the basic crystal and not for the activating metal. Band structure due to this origin has really been observed in the fluorescence spectra of some crystals activated by chromium or the rare earths (compare Table XX, page 188).

[12] T. Tanaka, *J. Optical Soc. Am.*, **8**, 287 (1924).

improbability would of course not invalidate reliable observations. However, Tanaka's measurements were made utilizing only a visual spectrophotometer; he did not record them objectively and no other author was ever able to repeat them. Thus it is almost certain that these regular frequency intervals do not exist and that they cannot be used for analysis.

The strong blue fluorescence of thallous salts in 4N hydrochloric acid or still better in a concentrated aqueous solution of NaCl is perhaps more promising as a test for thallium in small quantities.[13]* The fluorescence is excited by the short wave length ultraviolet radiation from an iron or aluminum spark. It is easily perceived at Tl concentrations of 10^{-7} molar. Like many other types of fluorescence it is strongly quenched by the presence of ferric ions in the solution.†

Notwithstanding the great number of data collected about the fluorescence of minerals, one does not see how qualitative fluorescence analysis can, beyond the few results mentioned in this paragraph, greatly benefit the mineralogist.‡ It is probable that by other methods of analysis and careful comparison of fluorescence properties the carrier of the luminescence in many of these minerals may be found as it was in the case of Willemite. But this will neither help to identify a mineral if the fluorescence is only "accidental," nor will it help to trace the same impurity in another mineral if the fluorescence spectrum is not an unequivocal characteristic of the impurity.

3. Qualitative Analysis in Organic Chemistry

For the separation of the higher polycyclic aromatic hydrocarbons, the observation of their fluorescence spectra has played almost the same part as for the separation of the rare earths. Many of these compounds (benzene, naphthalene, anthracene, naphthacene) have such characteristic fluorescence spectra that they are easily identified, even when

* Pb and Sn produce a much weaker greenish fluorescence under similar conditions. With Ag, Al, As, Au, Cd, Cu, Mn, Pt, Zn the results are completely negative.

† Concerning other fluorescence tests for different metals see page 107.

‡ The method of detecting Willemite (zinc silicate) and Scheelite (calcium tungstate) or distinguishing them from other minerals in zinc or tungsten mines, respectively, by means of their characteristic fluorescence is not to be called chemical analysis. It is one of the most important applications of fluorescence analysis for the identification of different materials which are treated in a subsequent section. It must be kept in mind that in the case of Willemite the fluorescence is not a property of the zinc ore as such. Many natural zinc silicates do not show this fluorescence. Whether some green fluorescing Willemites are really activated with uranium, as Spencer seems to suggest by the description of their brilliant "uranium-like fluorescence," seems rather doubtful.

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[13] P. Pringsheim and H. Vogels, *Physica*, **7**, 225 (1940).

superimposed upon each other.* The discrimination becomes more difficult if the bands of two components in a solution are located in the same region, as in the case of anthracene contaminated with carbazol. It becomes almost impossible if the bands, which are never very sharp, overlap, as in the case of most dyestuffs.

This difficulty is overcome by the use of the chromatographic method, which when combined with fluorescence analysis is sometimes called ultrachromatography.[14] It is based on the fact that the adsorption coefficient of a gel is frequently different for compounds which are similar in their chemical properties and cannot be separated by other means. From a solution of several compounds only one is adsorbed, as long as it is contained in the solvent. When its concentration has dropped to zero, the second compound is adsorbed, and so on. An adsorbent like silica gel or aluminum oxide is loosely packed in a narrow high glass cylinder and the solution is filtered through this column. From its upper to its lower end, the different compounds contained in the original solution are adsorbed in succession. They form annular zones on the adsorbent which were distinguished by their daylight colors only in the original method [15] Hence the method was useless if all the compounds were white. By the use of ultrachromatography all compounds are completely characterized by their fluorescence spectra under black light excitation.†

If two adjoining zones emit only ultraviolet fluorescence, a photographic record has to be employed. A solution of commercial anthracene in benzene produces along a column of aluminum oxide first a zone of carbazol with its deep blue fiuorescence, then the greenish fluorescent zone due to napthacene, and finally the undermost zone which shows the violet fluorescence of pure anthracene. In the same way many derivatives of anthracene like benzanthracene, dibenzanthracene, dinaphthanthracene and other polycyclic hydrocarbons and their heterocyciic impurities like benzcarbazol, brazene, etc., have been separated and identified.[16] Benzopyrene, contained in many natural coal tars, is of special interest because of its strong carcinogenic properties. The fluorescence spectrum of benzopyrene in different solvents has been studied, and it is sufficiently characteristic for

* Some heterocyclic compounds like coumarin and acridine and their alkyl substituted derivatives have similar characteristic spectra in solutions at low temperatures. At room temperature, however, the separated narrow bands fuse into one continuous band which is no longer suitable for a reliable analysis.

† The substances can be subsequently eluated from the adsorbent by appropriate solvents and thus they are isolated in pure form.

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[14] P. Karrer and K. Schopp, *Helv. Chim. Acta*, **17**, 693 (1934).

[15] M. Tswett, *Ber. deut. botan. Ges.*, **24**, 384 (1906).

[16] A. Winterstein and K. Schoen, *Z. physiol. Chem.*, **230**, 146 and 1158 (1934).

identification.[17] Even in a solution in hexane containing benzopyrene, dibenzanthracene, pyrene, retene, chrysogene, and phenanthrene, all at the same concentration of 10^{-5} molar, the fluorescence spectrum of benzopyrene prevails so clearly that it is recognized without difficulty. But in a coal-tar extract containing the same amount of benzopyrene the fluorescence spectrum does not betray a trace of the benzopyrene bands. Evidently these are not masked by other bands but are actually quenched by some basic component of the solution. After shaking the solution with sulfuric acid, the benzopyrene bands appear, but are rather weak and partially masked by other bands. They would hardly be sufficient for a reliable analysis without the use of the ultrachromatographic method.[18]

Methyl cholanthrene is another strongly carcinogenic hydrocarbon. Its fluorescence in alcoholic solution is blue. Ethyl and propyl cholanthrene, which are not carcinogenic, show a fluorescence of nearly the same intensity and color. The once supposed connection between the fluorescence of a compound and its carcinogenic properties is evidently nonexistent.[19]

The ultrachromatographic method has been used further for the separation of chlorophyll *a* and *b*, compounds which are chemically almost identical and which possess fluorescence spectra of similar structure with only slightly displaced bands (Fig. 40g and h, on p. 77). Uropterin, the yellow dyestuff contained in urine, was discovered and isolated by means of the same method.[20] Synthetic dyestuffs of similar chemical properties and similar daylight color contained in a mixture can also be separated and identified by ultrachromatography.*[21]

If its two constituents are not to be separated, chlorophyll, like some other natural dyestuffs mentioned in Table XIX, need not be treated by ultrachromatography for identification wherever it is present. The characteristic red bands are easily recognized in the fluorescence spectra of the leaves of living plants and of all kinds of plant extracts, oils, etc.

* An analogous but somewhat more primitive method known as "capillary analysis" has been used frequently, for instance for the fluorescence analysis of the alkaloids. A strip of filter paper is dipped into the solution and absorbs it by capillary forces. If a rapid evaporation of the solvent is not avoided by adequate precaution, formation of solid crystals of the dissolved substance might occur instead of the adsorption. The fact that in the case of the alkaloids several zones of different fluorescence colors were observed on the adsorbing paper, *e.g.*, blue and yellow ones for hydrastine, proves that the alkaloids were not pure, as supposed on page 76.

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[17] I. Hieger, *Biochem. J.*, **24**, 505 (1930); J. W. Cook, C. L. Hewett, and I. Hieger, *J. Chem. Soc.*, **1933**, p. 355; C. Sanne and V. Poremski, *Bull. soc. chim.*, **3**, 1139 (1936).

[18] G. Miescher, F. Almasy, and G. Klaeui, *Biochem. Z.*, **287**, 189 (1936).

[19] W. F. Bruce, *J. Am. Chem. Soc.*, **63**, 3041 (1941).

[20] W. Koschara, *Z. physiol. Chem.*, **A 240**, 127 (1936).

[21] J. Grant, *Textile Colorist*, **62**, 9 (1940).

Most commercially prepared chlorophyll, however, is not fluorescent, either because it is in the colloidal state or because the nature of the dye has been altered by some chemical treatment.

The different kinds of porphyrins are identified by observation of their fluorescence spectra* in the yolk and the shells of eggs as protoporphyrin[22] and hematoporphyrin, in the bones of newborn animals as coproporphyrin, in certain glands of animals as protoporphyrin, in urine as copro- and uroporphyrin, in the bacilli of tuberculosis and diphtheria,[23]† in yeast, etc., and in the organisms themselves as well as in extracts. In alcoholic solution the fluorescence of hematoporphyrin is still perceived with certainty at concentrations below 10^{-7}. Other dyestuffs of similar type, like bonellin, phycocyanin, or phylloerythrin, are so far important only for special scientific research work.[24] On the other hand, much interest has been bestowed lately on the fluorescence of vitamins, hormones, enzymes, etc. Among the vitamins only vitamin B_2 (riboflavin, lactoflavin) has, in liquid solutions, a fairly strong fluorescence emission of its own which could be made useful for qualitative and quantitative analysis. The greenish yellow luminescence can also be observed in milk, butter and in plant extracts. When adsorbed on colloids the dye is not fluorescent. The emission spectrum shows a broad symmetric band from 5000 to 6000 Å with maximum at 5620 Å[25] and is hardly sufficiently characteristic for a discrimination between the vitamin and some other dyestuff with a yellow-green fluorescence like trypaflavine which is chemically not at all related to riboflavin. A very characteristic property of the riboflavin fluorescence, however, differentiates it very clearly from other dyestuffs. Under the action of the exciting light the fluorescence color turns from greenish yellow into light blue, the flavine being converted by a photochemical process into lumichrome (trimethyl-isoalloxazine), if the solution is neutral or slightly acidified, or into lumiflavin (6,7-dimethyl-alloxazine), in alkaline solutions. By its sky-blue fluorescence lumiflavin is easily distinguished from its isomeres: under the same experimental conditions 6,8- and 7,8-dimethyl-alloxazin show a bluish green fluorescence and 5,8-dimethyl-alloxazine a greenish yellow fluorescence.[26]

* For a non-spectrometric method of discrimination between the different porphyrins, compare page 114.

† The fluorescence spectra of these bacteria show, in addition to the narrow porphyrin bands a broad continuous band covering the whole visible region from orange to violet. This fluorescence is due to some other constituents.

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[22] Ch. Dhéré, *Compt. rend. soc. biol.*, **112,** 1595 (1933); A. Stern and M. Deželić, *Z. physik. Chem.*, **A 177,** 347 (1936).

[23] Ch. Dhéré and L. Ropetti, *Bull. acad. méd. Paris*, **114,** 96 (1934).

[24] F. Roche, *Arch. phys. biol.*, **10,** 91 (1933).

[25] P. Karrer, H. Salomon and others, *Helv. Chim. Acta*, **17,** 1010 (1934).

[26] P. Karrer and C. Musante, *ibid.*, **18,** 1134 (1935).

Most of the other vitamins, like vitamin C (ascorbic acid), vitamin E (tocopherol), many hormones, ferments and other compounds important for biological processes are known to be photoluminescent but the knowledge of their luminescence is not yet sufficiently advanced so that it could serve for analytical purposes.

Vitamin A in liquid solutions exhibits a greenish fluorescence, the constancy of which depends on various conditions. In alcoholic solutions the fluorescence intensity of vitamin A esters, such as the acetate, oleate, etc. drops under the action of the exciting radiation after an initial increase almost to zero. The initial and the peak intensities are proportional to the vitamin concentration. The change in intensity is due, at least partially, to a photosensitized reaction with oxygen, since it is greatly reduced if CO_2 is bubbled through the solution flushing out the oxygen.* The behavior of the free vitamin A alcohol is essentially different; its initial fluorescence is the same as that of an equivalent concentration of the acetate, but it decreases immediately from the beginning of the irradiation without showing an initial rise. Thus, by observing the change of fluorescence intensity of an alcoholic vitamin A solution with time one can determine the relative concentrations of free vitamin A alcohol and of vitamin A esters in the solution.

A similar "fading green fluorescence" is produced by the presence of vitamin A in certain organisms. Although it seems that this fluorescence has not yet been used for routine quantitative analysis, it offers a means of studying the distribution of vitamin A within the different organs of an animal under varying conditions.[27a]

Vitamin B_1 (thiamin or aneurin) is not fluorescent itself, but it can be converted by a simple chemical reaction into a strongly fluorescent dye called thiochrome.[27b] This procedure provides an example of another type of fluorescence analysis which can be useful when the substance to be identified is not luminescent and even when the fluorescence spectrum of the final product is not very characteristic. The chemical reaction itself is frequently sufficiently specific.

In the case of vitamin B_1, the vitamin is dissolved in water and oxidized into thiochrome by addition of potassium ferricyanide. About 67% of the thiamin present in an organism is converted into thiochrome by the

* The solvent, alcohol, plays apparently an important part in this process of photo-oxidation. When vitamin A acetate is dissolved in benzene, its fluorescence remains at a nearly constant level over a relatively long period, while the solubility of oxygen is somewhat larger in benzene than in alcohol.

† Compare this chapter, section 8.

[27a] H. Sobotka, S. Kahn and W. Winternitz, *J. Biol. Chem.*, **152**, 635 (1944). H. Popper and R. Greenberg, *Arch. Path.*, **32**, 11 (1941).

[27b] G. Barger, F. Perger, and A. R. Todd, *Nature*, **136**, 259 (1935); B. C. P. Jansen, *Rec. trav. chim.*, **55**, 1046 (1936).

usual method. When subsequently the thiochrome is extracted from the aqueous solution by butanol, it emits a strong blue fluorescence under black light excitation.[28]

Neither the red blood dye hematin* nor the bile dyestuffs bilirubin and urobilin are fluorescent. In the former the potential fluorescence is quenched by the iron contained in the complex molecule. If the iron is removed by the action of sulfuric acid,[29] or rather by some weak organic acid like formic acid in the presence of a reducing agent, hematin is converted into hematoporphyrin with its typical red porphyrin fluorescence.[30]

The bile dyestuffs become fluorescent when their molecules are converted into zinc complexes by addition of a zinc salt, *e.g.*, zinc acetate to an alcoholic solution of the dye.† The fluorescence is red in the case of bilirubin and green in the case of urobilin. Of all biological fluorescence phenomena this strong green fluorescence of the zinc-urobilin complex is certainly the one that has been known longest and has been most frequently used for medical analyses.[31]

A good many chemical conversions into fluorescent compounds have been recommended by different authors for the identification of non-fluorescent organic compounds. The method has the advantage that it needs very small quantities of material and can often be carried out in so-called spot tests. For instance, a dark stain on a piece of cloth may be recognized as blood if it becomes fluorescent after it has been moistened with a drop of acetic acid and another drop of a solution of sodium thiosulfate. The usual technique for fluorescent spot reactions is first, to place a drop of the solution to be analyzed on a piece of filter paper and, when it is soaked in, to add on top of it a few drops of the different chemicals needed for the reaction. The spot is thereupon exposed to the radiation of a "black lamp."

Dicarboxylic acids, heated with resorcinol and concentrated sulfuric acid, form dyes of the fluorescein type. The same treatment applied to hydroxydicarboxylic acids produces dyestuffs of the umbelliferone type. The former shows a green, the latter a blue, fluorescence in alkaline solutions. Though the color of the fluorescence is not quite the same for different acids, the contrasts are hardly sufficient to differentiate between the green fluorescent products derived from phthalic, succinic, tricarboxylic acids and saccharin, or between the blue fluorescent products of citric and malic acid.

When aliphatic amines, amides or imides such as methylamine, hydrox-

* In hematoglobin hematin is associated with a protein.

† The mercury complexes of these dyestuffs are also fluorescent.

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[28] R. T. Conner and J. Straub, *Ind. Eng. Chem., Anal. Ed.*, **13**, 380 (1941).

[29] M. Wagenaar, *Z. anal. Chem.*, **79**, 107 (1929).

[30] Ch. Dhéré, *J. physiol. path. gén.*, **16**, 67 (1917).

[31] M. Jaffé, *Zentr. f. med. Wiss.*, **7**, 177 (1929).

ylamine, hydrazine, semicarbazide, saccharin, and piperidine are fused with fluorescein chloride and zinc chloride, symmetric rhodamines* are formed which are dialkyl substituted in the case of primary, tetra-alkyl substituted in the case of secondary amines, etc. The former show a yellow-green, the latter an orange fluorescence in acidified solutions. The same treatment of aromatic amines leads to the production of aryl-substituted rhodamines which are not fluorescent. On the other hand yellow fluorescent rhodamines result from the reaction if the aliphatic amines are replaced by inorganic ammonium compounds like ammonium chloride.

Some reactions have also been found by which alkaloids are converted into compounds which fluoresce strongly in solution. These probably constitute more reliable tests than the mere examination of the fluorescence of the solid alkaloids themselves. Thus morphine, heated with concentrated sulfuric acid to 40° C. and, after cooling, diluted with water and ammonia, turns into a solution which after some time develops a strong purple fluorescence. By this test morphine can be distinguished from pseudo-morphine and from codeine but not from heroin.[32]

The existence of a great number of different organic substances which after identical chemical treatment give rise to fluorescence emissions which can scarcely be distinguished from each other shows that the method will be useful only when combined with other tests.† In the case of the fluorescein chloride-rhodamine reaction, the appearance of the fluorescence seems to prove not much more than that a NH_2 or NH group is present in the compound and that it is not an aromatic amine. The same criticism is probably to be applied to other tests of the same kind for lactic or tartaric acid, glycerol, allyl alcohol and many other substances. From any organic compound some fluorescent substance may be derived somehow. The question is whether other compounds might not produce a similar fluorescence after having undergone the same procedure. Such tests are of course very valuable if the problem is only to ascertain whether a certain compound is or is not present in a solution.

A typical example of this kind is provided by a reaction which has been repeatedly described as a test for the presence of sulfur dioxide. In this process SO_2 is oxidized to H_2SO_4 and the sulfuric acid identified by the strong blue fluorescence which it causes in a quinine solution. This is quite correct but hardly very specific, since any acid may convert quinine

* Formulae for various rhodamines are to be found in Table XVIII at the end of the volume.

† Occasionally such a second test may be provided by the body color of the reaction product. For instance, the rhodamine solutions resulting from the treatment of aliphatic amines described above all show nearly the same yellow fluorescence, but in daylight some of them are pink and others red or orange. In other cases such differences of daylight color do not exist.

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[32] C. C. Fulton, *J. Am. Pharm. Assoc.*, **26**, 726 (1937).

in an aqueous solution into its strongly fluorescent divalent ion. As a matter of fact the method was recommended by Grant and Booth not as a general test for the presence of sulfur dioxide but as a test for the presence of SO_2 in milk, to which it is sometimes added as a preserver.[33a] In this special case it may be improbable that another impurity would produce the same result, in so far as milk contains no lactic acid.

Dihydro-acridine in alcoholic solution is oxidized by ozone into acridine which is easily identified by its intense violet fluorescence, while the hydrated compound is not fluorescent. By this method ozone concentrations down to 10^{-11} g. per cc. can be ascertained. This corresponds to a concentration of about $10^{-6}\%$ of ozone in atmospheric air. Oxygen itself or hydrogen peroxide has no effect. However, dihydro-acridine is strongly oxidized by the different nitrogen oxides; if they are present they must be removed before the ozone test can be applied.[33b]

Some reactions of organic compounds in which a metal participates may be used as well for the identification of the metal. The green fluorescence of the urobilin-zinc complex is a test for the presence of zinc. The complex precipitated from a zinc salt solution by addition of 8-hydroxy-quinoline shows a strong yellow-green fluorescence which is supposed to be easily distinguished from the blue-green fluorescence characteristic of the complexes which are precipitated by other metals like Ca, Sr, Th, and Mn. The Cd complex is recognized by its pure green fluorescence. At a concentration as low as 10^{-6}, zinc can still be identified by this reaction.[34] Aluminum salts in neutral or alkaline solutions and beryllium salts in acidified solutions form complex molecules with morin ($C_{15}H_{10}O_2$), both conspicuous by their bright green fluorescence. These morin tests are very selective; of all other metals only Li, Ca, Zn and Sc produce a similar but much weaker fluorescence in morin solutions. The morin test for Al and Be can be used in spot tests with quantities of 10^{-8} g.[35]

Even more definite tests for Al and Be are the following: Aluminum at concentrations as low as 1×10^{-7} gives rise to an orange-red fluorescence with an emission band 6365–6975 Å, when introduced into an ethanolic solution of Pontochrome blue black R (du Pont) at a temperature of 80° C.* A similar red fluorescence[36] is produced in alkaline solutions of 1-amino-4-hydroxy-anthraquinone by addition of a beryllium salt at

* In aqueous solutions at room temperature the formation of the luminescent complex takes some time.

[33a] J. Grant and I. H. W. Booth, *Analyst*, **57**, 514 (1932).

[33b] M. Konstantinova, *Acta Physicochim. U. R. S. S.*, **3**, 435 (1935).

[34] J. Eisenbrand, *Pharm. Z.*, **75**, 1033 (1930).

[35] E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 712 (1940); H. L. Zermatten, *Proc. Acad. Sci. Amsterdam*, **36**, 889 (1933).

[36] C. E. White and C. S. Lowe, *Ind. Eng. Chem., Anal. Ed.*, **9**, 430 (1937) and **13**, 810 (1941).

beryllium concentrations down to 4×10^{-7}. In acidified solutions of the same compound (pH = 2) a stable colloidal suspension is formed by addition of a thorium salt, showing a strong purple fluorescence. This test is somewhat less sensitive (the lower limit is about 10^{-5}, 40 γ in 5 cc.), but it is also perfectly selective.[37]

Another test of this kind, precipitation of sodium uranyl acetate by addition of uranyl acetate to a sodium salt solution, can hardly be admitted as sufficiently specific if not combined with an exact spectrometric analysis. There are too many uranyl compounds with almost identical fluorescence properties. The D-line emission of all sodium compounds in a Bunsen flame is probably a much safer and certainly a simpler proof of the presence of sodium.

4. Purity Tests

A reversal of the problem treated in the preceding paragraphs is the proof of the purity of a material by the total absence of luminescence, by the absence of certain fluorescence bands in the luminescence spectrum, or by the absence of an afterglow. Such purity tests should always be executed with photoexcitation because, as mentioned before, cathode rays or x-rays frequently produce new "luminescence centers" in non-luminescent substances. The same is even true for long exposure to ultraviolet light.

It may happen that absence of fluorescence is due to the presence of a quencher and thus is no conclusive proof for purity.*

If the test in question is to be repeated as routine work, it is advisable to procure a sample of the greatest purity and to compare it with the sample under investigation. As explained on page 68 "total absence of fluorescence" is a somewhat elastic notion. In a solution a faint fluorescence of the solvent may interfere, diffusion of the primary light may not be completely screened off, and so on.

In many even quite recent publications the visible fluorescence of naphthalene, fluorene, phenanthrene, chrysene, cyclohexane at room temperature is described. This is a proof that the materials employed in these experiments were not pure. The best phenanthrene manufactured by Kahlbaum contains several per cent of anthracene,[38] enough so that even in dilute alcoholic solutions or in the vapor the violet anthracene bands show up clearly.[39] The hydrocarbons which Berthelot named fluorene because of its beautiful blue fluorescence[40] and chrysene, the "golden one," owe their names to qualities produced by impurities: anthracene and

* A small contamination with copper produces strong phosphorescence in pure CaS. Added traces of iron quench the phosphorescence completely.

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[37] C. E. White and C. S. Lowe, *Ind. Eng. Chem., Anal. Ed.*, **12**, 712 (1940).
[38] S. Sambursky and G. Wolfsohn, *Trans. Faraday Soc.*, **36**, 427 (1940).
[39] P. K. Seshan, *ibid.*, **32**, 689 (1936).
[40] B. Twarowska, *Z. Physik*, **109**, 403 (1938).

carbazol in the first and naphthacene in the second case. Both are white when pure, and fluorene has only U.V. fluorescence bands.[16] All commercial anthracene is contaminated with several per cent of naphthacene. The better grades contain at least 0.1% naphthacene and even the best analytical grade of anthracene contains 10^{-5}% naphthacene. Even with a concentration of 10^{-6}% the green-yellow fluorescence of napthacene outshines the violet fluorescence of the main substance.*[16]

A very characteristic blue fluorescence is observed at low temperatures in many organic paraffins as well as benzene derivatives like the xylenes. The spectra always consist of several narrow bands in the blue to violet region; they are ascribed by Terenin to aldehydes produced in the compounds by auto-oxidation.[41] Similar impurities may be the carriers of fluorescence in other organic compounds even at room temperature, since in many cases the fluorescence intensity decreases with progressing purification.

Alkaline aqueous solutions of purines and pyrimidines like xanthine, uracil, adenine sulfate, isocytosine, etc., occasionally show a strong yellow fluorescence which disappears completely after repeated recrystallization of the compounds. The pure substances are characterized only by a much weaker bluish luminescence.[42]

It has already been mentioned that most inorganic salts become luminescent after addition of very small impurities. It is very difficult to decide how far the proper fluorescence of such salts as listed in most books is really genuine. Aluminum oxide, for instance, is supposed to show a pink fluorescence. In this case it was proved by Boisbaudran and by G. C. Schmidt that the pure salt is not luminescent at all and that the pink fluorescence is due to the last traces of chromium oxide. Many inorganic crystals which are not luminescent at room temperature are excited to a strong fluorescence at liquid air temperature even by black light. Such substances are, according to Randall, barium sulfate, cadmium bromide, lead chloride, silver chloride, thallium chloride and others. If this light emission should also prove to originate from impurities, it is clear that the examination at low temperatures would provide a still more sensitive test for purity than the normal procedure.[43]

It is not quite settled whether the sulfides of the alkaline earth metals,

* A sample of synthetic anthracene prepared in the laboratory of Professor Dufraisse, which was kindly given to me for further investigation in a carefully sealed off glass tube showed unmistakably by the fluorescence test that it contained a contamination of naphthacene. Fractional crystallization or sublimation is not satisfactory for the purification of this compound, and this is evidently the reason for so many erroneous results.

[41] A. Terenin, *Acta Physicochim. U. R. S. S.*, **12**, 617 (1940) and **13**, 1 (1940).
[42] M. M. Stimson and M. A. Reuter, *J. Am. Chem. Soc.*, **63**, 697 (1941).
[43] J. T. Randall, *Trans. Faraday Soc.*, **35**, 1 (1939).

which constitute the bases of the most powerful phosphors, are fluorescent when absolutely free of any impurity. It seems to be rather improbable. At any rate they are not phosphorescent. An admixture of a heavy metal like Cu or Bi at concentrations of less than 10^{-7} gives rise to a long-lasting afterglow. In pure zinc sulfide a short afterglow may be observed during one or two minutes. Long-lasting phosphorescence is indicative in this case also of the presence of an impurity. The fluorescence of pure calcium tungstate has a decay period of the order of thousandths of seconds. Contamination with lead or arsenic causes an easily observable afterglow. Such tests are important for the selection of the material to be used in the preparation of well-determined phosphors.

Certain dyestuffs like trypaflavine are able to emit a phosphorescence lasting several seconds when they are adsorbed on silica gel and kept in a high vacuum. This afterglow is quenched by oxygen at partial pressures below 10^{-4} mm.Hg, while the fluorescence is practically unaffected. Other permanent gases like nitrogen, hydrogen, or carbon dioxide, which might be present, do not interfere with the phosphorescence. The method provides, according to Kautsky, an exceedingly simple and quite selective test for the presence of traces of oxygen.[44]

The same principle has been recommended by different authors for proving the presence of certain ions like I^-, Br^-, or $S_2O_3^{--}$ by their quenching action upon the fluorescence of uranyl salts in solutions. The quenching action of many substances in fluorescent solutions discovered by Stokes has been studied since, both qualitatively and quantitatively, by many physicists. The presence of some quenching impurity can be inferred from a too low fluorescence yield. However, the matter is so complex, and the quenching substances are so numerous, that it would certainly be quite impossible to draw any conclusions respecting the nature or the concentration of a quencher from the mere fact that the fluorescence of a solution has an intensity below its normal value. Volmar who is quoted frequently as the inventor of this method never presumed anything of the kind.[45] He states only that it might be possible to determine the concentration of a KBr or a NaCNS solution by measuring its quenching action on the fluorescence of a uranyl nitrate solution.*

5. Quantitative Analysis

The sensitivity of fluorescence analysis is in some cases probably surpassed only by radioactive tests, and therefore quantitative fluorescence

* If the concentration of the quenching solution is known, it would, according to Volmar, be possible to deduce the nature of the quenching ion from the decrease of fluorescence intensity on addition of a certain number of drops of the solution. However, this hardly seems to be a very useful method.

[44] H. Kautsky, *Z. anorg. allgem. Chem.*, **222**, 126 (1935); J. Franck and P. Pringsheim, *J. Chem. Phys.*, **11**, 21 (1943)

[45] Y. Volmar and Martin, *Bull. soc. chim.*, **53**, 385 (1933).

analysis could yield excellent results over very wide concentration ranges. However, it is under no circumstances serviceable for the activating impurities in inorganic phosphors and not even for organic compounds in solid solutions as in boric acid or sugar. In all these cases the luminescence intensity depends on too many factors which are not connected with the concentration of the luminescent molecules. In liquid solutions in a well-defined solvent and at a well-defined temperature the results of the measurements could only be made ambiguous by the presence of quenching substances or of other fluorescent compounds. If the latter difficulty cannot be avoided for technical reasons, and if the interfering fluorescence has a different spectral distribution or is excited by light of other wave-lengths, the use of adequately colored filters in the path of the exciting or the fluorescent light may be helpful.

It is not possible to obtain reliable quantitative results by simply measuring the ratio between the fluorescence intensity of the solution under investigation and of another solution of known concentration. For the reasons stated in Chapter II it can by no means be taken for granted that this ratio is equal to the ratio of concentrations.* All corrections necessary because of the reasons already mentioned or because of unequal illumination of the two samples or incomplete symmetry of the photometer itself cancel out if the photometer is calibrated by matching a set of solutions of known concentrations against the intensity of a constant "comparison solution." The concentration of any other solution can then be determined by interpolation. Thus only equal or nearly equal solutions are compared with each other. The same purpose is of course attained by diluting either a standard solution or the solution under investigation until the luminescence intensities of both are equal. As the observed fluorescence intensities of a solution may pass through a maximum at a certain concentration (Fig. 12) it must be ascertained that both solutions are on the same side of the maximum. In general it will be the side of the smaller concentrations. It is self-evident that the same solvent must be used for all solutions to be compared, since the fluorescence yield of all compounds is greatly dependent on the nature of the solvent.

Every one of the photometers described in Chapter III may be employed for these measurements. Without the use of any photometer Karrer compared the brightness of two fluorescent solutions by putting them side by side in the field uniformly illuminated by an "analytic lamp" and diluting the one until equality of brightness seemed to be reached.[47] Even by

* Pages 25 and 55. Quantitative capillary analysis, based on the measurement of the fluorescence intensity of hydrocarbons which have been adsorbed on filter paper from a given quantity of liquid solution should produce results even less reliable than intensity comparisons in liquid solutions.[46]

[46] F. E. E. Germann and J. W. Hensley, *J. Phys. Chem.*, **44**, 1071 (1940).
[47] W. Karrer and U. Kubli, *Helv. Chim. Acta*, **20**, 369 (1937).

means of this rather rough comparison, he was able to find the thiochrome content of a solution with an average error not surpassing 20%. An objection proffered against these measurements is not really directed against the method of fluorescence analysis. It seems that the results were only satisfactory with synthetically prepared solutions. With natural products, however, the fluorophotometric results were in general 30–50% below those of biochemical assays. With yeast preparations the fluorescence analysis gave a completely negative result, though the preparations contained considerable amounts of vitamin B_1.[48] This discrepancy was caused by an imperfect mode of extracting the vitamin from the natural products, while the analysis of the solutions was quite correct. As a matter of fact, methods developed since for the extraction of thiamin provide thiochrome solutions which give in all cases a very satisfactory agreement between biological and fluorometric tests. 2.9 micrograms of thiamin chloride are equivalent to 1 I.U. (international unit in biological test). The use of a sensitive photometer allows the accurate determination of 0.1 microgram of vitamin B_1. The whole procedure of the fluorometric analysis can be performed within a few hours while the biological rat test takes at least five days.[49]

The most frequent use made at present of quantitative fluorescence analysis is concerned with the vitamin B_2 content (riboflavin or lactoflavin) of foodstuffs and other material. Fluorophotometers, constructed in increasing number by optical firms, are advertised chiefly for this purpose. Many liquids which are to be tested for the vitamin contain other fluorescent components apart from riboflavin. Therefore the yellow-green fluorescence of the vitamin is isolated from the fluorescence of the other substances, which is generally of shorter wave-lengths, by means of an orange-yellow screen. Blue light, *e.g.*, the blue Hg line 4358 Å, is most effective for excitation. Near U.V., transmitted through a Wood filter, would not be advisable in this case for, while the riboflavin fluorescence is little stimulated by it, the fluorescence of most other impurities would be excited to great intensities. Table XII shows the fairly good agreement between different biological and fluorophotometric tests for vitamin B_2.[50] The units are micrograms of vitamin B_2 per gram of substance. The limit of sensitivity of the fluorescence analysis for riboflavin is 5×10^{-3} micrograms per cubic centimeter. A volume of about 10 cubic centimeters is the minimum quantity required for a test. Vitamin B_2 can be extracted from milk without loss by 66% acetone, the extract being filtered subsequently.

[48] M. Pyke, *Nature*, **141**, 1141 (1938).
[49] D. J. Hennessy and L. R. Cerecedo, *J. Am. Chem. Soc.*, **61**, 179 (1939).
[50] R. T. Conner and J. Straub, *Ind. Eng. Chem., Anal. Ed.*, **13**, 385 (1941).

The normal riboflavin content of milk is found by fluorescence analysis to vary from 1.2 to 3.4 mg. per liter.

Fluorescence tests for vitamins B_2 and B_1 can be made from one and the same plant extract, by passing the solution at first through a column of Delcalse (a synthetic zeolite) which adsorbs only the thiamin content, and then through a column of Supersorb (a special kind of fuller's earth)* which adsorbs the riboflavin and from which the latter can be re-eluated completely by a mixture of pyridine and acetic acid.[51]

The great sensitivity causes the main difficulty in practical application of quantitative fluorescence analysis for liquids like serums, urine, or any extracts from living organisms. In almost every case the fluorescence or the quenching effect of some other compound contained in the liquid will

TABLE XII

VITAMIN B_2 ANALYSIS

Substance	Biological tests		Fluorophotometric tests.	
	Rat test	Yeast fermentation	Photocell	Visual
Wheat germ extract	4.5	3.2	2.7	3.7
Yeast dried	62.0	46.0	51.0	65.0
Yeast concentrate	200.0	171.0	192.0	195.0
Liver extract	500.0	501.0	507.0	537.0
Wheat germ special concentrate	942.0	940.0	965.0	934.0
Special concentrate	4690.0	4610.0	4900 0	4750.0

interfere. For the test of compounds with red or even yellow fluorescence the filter method can be helpful. In general, however, the problem to be solved will be a quantitative extraction of the substance under investigation. If this can be done satisfactorily, as in the case of thiamin, the quantitative analysis by fluorophotometry itself is a rather easy task yielding reliable results even at very low concentrations.

Fluorophotometry is peculiarly appropriate for the converse problem, the exact dosing of a fluorescent substance in a solvent of known quality. The same is true for the dosage of a quenching agent if one is sure that no other quencher is present. The method may be very useful for the quantitative determination of exceedingly small amounts of oxygen added to another gas by its effect upon the phosphorescence of dyestuffs adsorbed on silica gel.

* Adsorbates on activated charcoal give very erratic results.

[51] A. F. Emmett, O. D. Bird, R. A. Brown, G. Peacock, and J. M. Vanderbelt, *Ind. Eng. Chem., Anal. Ed.*, **13**, 219 (1941).

6. Fluorescent Indicators

If a fluorescent compound is ionized in a solution, its state of ionization depends on the *p*H of the solvent. With the passage from one ionic state to another, as represented by the symbols: A^{++}—A^{+}—A—A^{-}, the fluorescence of the compound changes either its color or disappears completely. A few examples may prove that there is no general law regarding the state of ionization which is most favorable for fluorescence. The fluorescence of the negative fluorescein ion in alkaline solutions is very strong and of yellowish green color, the band maximum being at 5170 Å. In a neutral solution it becomes very weak and almost colorless. In an acidified solution (*p*H-4), positive ions are formed, emitting a fairly bright blue-green fluorescence with the band maximum at 4800 Å.[52] The porphyrins also show two different fluorescence spectra in alkaline and acidified solutions with a very pronounced minimum of intensity at the isoelectric point*[53] (Fig. 45). In other cases the fluorescence is strongest in neutral solutions. The emission of riboflavin, of lumichrome, and of alloxazin has its maximum in the *p*H region between 3 and 9, where according to Kuhn the molecules are electrically neutral in the form of zwitter ions. The positive or negative ions prevailing in strongly acid or alkaline solutions show no visible fluorescence (Fig. 46). However, the secondary hump of the riboflavin curve, Figure 46, at *p*H=3.5, suggests that in this case also the molecules exist in two different states of ionization in the *p*H region between 3 and 9.[54] The same assumption is made even more plausible by the curves 2 and 3 of Figure 46, which represent the behavior of alloxazin, the dyestuff of which riboflavin is a derivative. Karrer[55] measured the intensity of the fluorescence transmitted through two different color screens and it is quite evident that while the blue fluorescence reaches its maximum intensity at about *p*H=4.5, the curve for the fluorescence viewed through the green glass has a peak near *p*H=8. If the transmission bands of the two screens and the emission bands of the two ionic modifications would not overlap, the two curves would probably be still more distinctly separated. At any rate this example proves that mere intensity measurements without regard to a possible color shift are apt to yield rather equivocal results.

* For different porphyrins the point of minimum fluorescence intensity is located at different *p*H values. Fink and his collaborators devised a method for the identification of the various porphyrins based upon this fact. For the difference between the "alkaline" and the "acid" porphyrin spectra see Table XIX. The fluorescence color is red in the first case and orange yellow in the second case.

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[52] G. N. Lewis and Th. T. Magel, *J. Am. Chem. Soc.*, **63**, 3005 (1941).
[53] Ch. Dhéré, A. Schneider and Th. van der Bom, *Compt. rend.*, **179**, 351 (1924).
[54] R. Kuhn and G. Maruzzi, *Chem. Ber.*, **67**, 888 (1934).
[55] P. Karrer and H. Fritsche, *Helv. Chim. Acta*, **18**, 911 (1935).

The fluorescence of the non-ionized acridine molecule in neutral or alkaline solutions is blue violet, while the fluorescence of the positive acridine ion in acidified solutions with *p*H 5 is green; both have about the same intensity.[56] In the case of quinine sulfate the electrically neutral molecule is stable in alkaline solutions of *p*H 9.5. It is only very slightly fluorescent ("colorless"). In solutions of *p*H from 9.5 to 6 the singly charged positive ions predominate and the fluorescence is violet, changing into a much brighter whitish blue when doubly charged positive ions are formed in acidified solutions.[57]

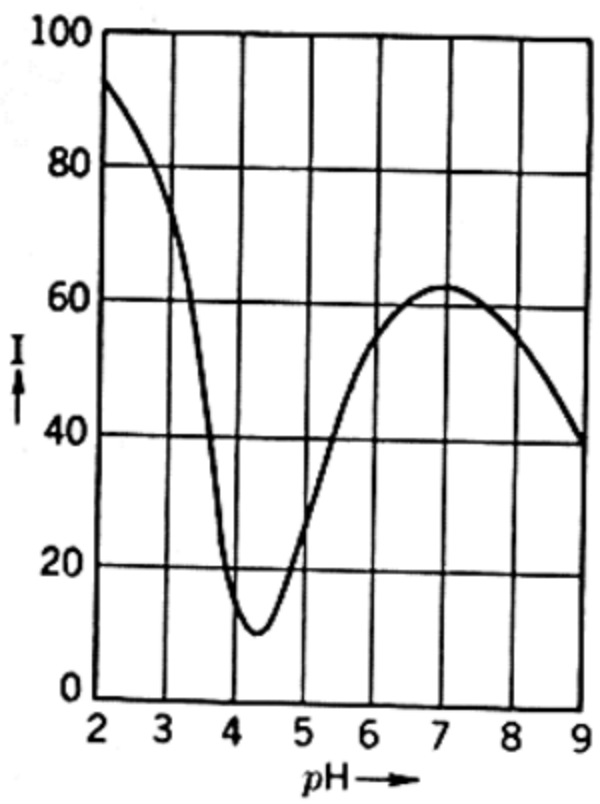

Fig. 45.—Fluorescence intensity in arbitrary units as function of *p*H. Hematoporphyrin.

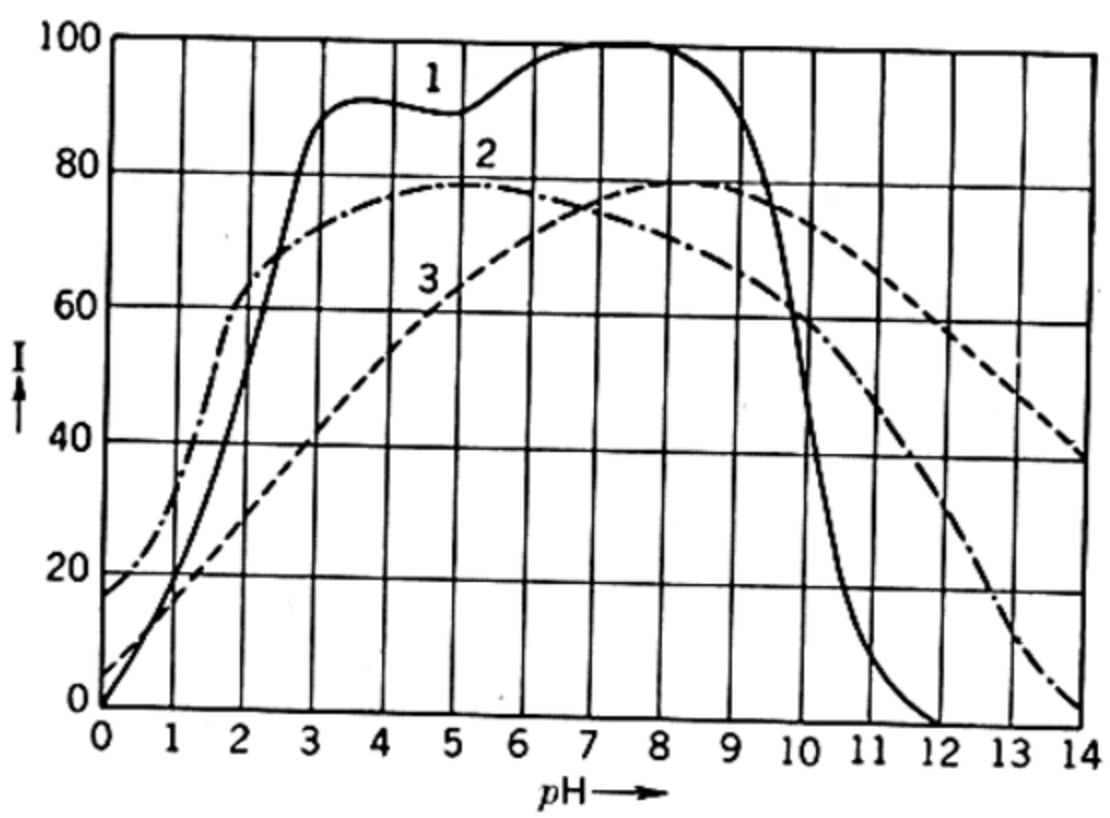

Fig. 46.—Fluorescence intensity in arbitrary units as function of *p*H.
1: Riboflavin (Kuhn and Maruzzi).
2: Alloxazin viewed through blue screen.
3: Same viewed through green screen (Karrer).

The same differences of fluorescence are observed when the compounds are adsorbed on gels of different polarity. This has, for instance, been demonstrated by Bandow for the two types of fluorescence spectra emitted when a porphyrin is adsorbed either from an alcoholic solution on Al_2O_3 or from an acidified solution on silica gel.[58] If quinine sulfate is adsorbed on silica gel from a neutral or an acidified solution, the fluorescence of the adsorbed substance always shows the same whitish blue fluorescence color. The doubly charged quinine ions, which are present also in the neutral solution, although in small concentration, are preferentially adsorbed by

[56] Y. Volmar and E. Widder, *Chimie & industrie*, **21**, 160 (1929).

[57] J. Eisenbrand, *Pharm. Ztg.*, **75**, 1033 (1930); W. N. Hartley, *J. Chem. Soc.*, **A 63**, 243 (1893).

[58] F. Bandow, *Z. physik. Chem.*, **B39**, 1555 (1938) and **B42**, 67 (1939).

the negatively polar gel, and they are again re-formed in the solution according to the equilibrium concentration.*

Since the relative number of two kinds of ions contained in a solution varies steadily with varying *p*H, and since in general the emission bands of both ions are broad and diffuse, an erroneous impression is frequently produced. The peak of the band seems to be shifted steadily.[59] Only when the spectra of both ionic states consist of a series of narrow bands does it appear clearly that one set of bands is weakening while the other grows stronger.†

Every substance, the fluorescence of which changes in color or intensity with varying *p*H of the solution, can be used as an indicator for the acidity of the solvent. It will be the more appropriate the more the color changes rapidly with increasing *p*H. An exact determination of the fluorescence color of a single indicator dyestuff would allow the determination of the *p*H values of a solvent over a large range of steadily changing colors. Measurements of the relative fluorescence intensities transmitted through three color screens would provide such a determination, and, according to Haitinger, *p*H values can thus be found with an error below 0.1. However, curves showing the *p*H values as a function of fluorescence intensity and color saturation have been published so far only for quinine (*p*H 5–9) and phosphin 3R (*p*H 3–5) (Fig. 47).‡ Besides the method is probably too complicated for normal routine work.

Long lists of fluorescent indicators have been compiled. The selections of indicators seem to be somewhat fortuitous and might probably be improved a good deal. Fluorescein and eosin, for instance, are listed only as indicators for acid solutions with *p*H = 4–4.5 and *p*H=2.5–4.5 respectively. The appearance of the positive ion fluorescence at these *p*H values is by no means very striking. The turning points on the alkaline side due to the formation of the negative fluorescein or eosin ions is much sharper. A great number of naphthalene and acridine derivatives seem to be especially favorable. Some of them are included in Table XIII, which con-

* This is probably the principal reason for the difference in fluorescence color shown by different textiles dyed with the same dyestuff. For instance, when dyed on cellulose acetate rayon the fluorescence of thioflavin is blue. It is yellow on viscose rayon. On silk it is green, probably by superposition of the two other colors. To a certain extent the fluorescence color also depends on the concentration of the dyestuff because of a partial reabsorption of the fluorescent radiation in the colored material. Finally small shifts of the peak of the fluorescence band are caused by a direct action of the solvent or the adsorbent on the molecules of the dyestuff (see p.76).

† This was proved by unpublished experiments on the fluorescence of acridine in alcoholic solutions at liquid air temperature with stepwise addition of hydrochloric acid.

‡ Haitinger, *Die Fluoreszenzanalyse in der Michrochemie*, p. 179.

[59] A. Schoentag and H. Fischer, *Z. physik. Chem.*, **B39**, 411 (1938).

tains a restricted selection of the supposedly best indicators covering the whole range from pH = 0 to pH = 13.

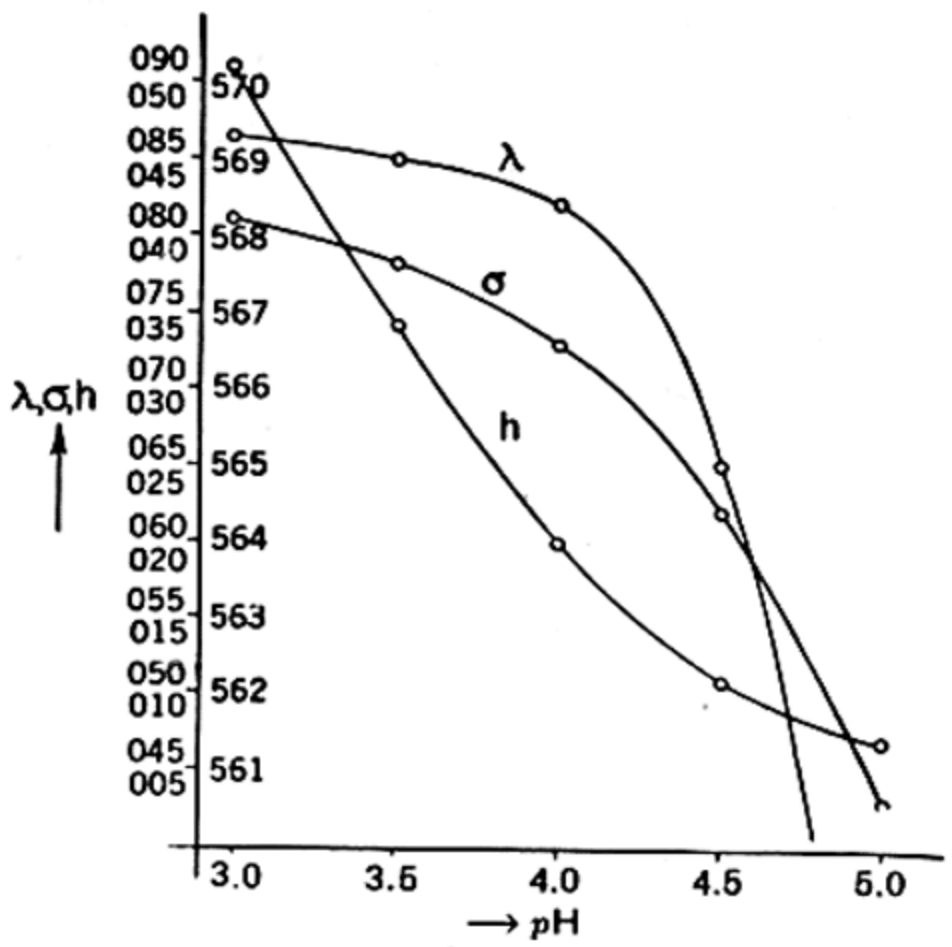

Fig. 47.—Phosphine 3R as fluorescent indicator: intensity, color, and color saturation as function of pH (Haitinger).

TABLE XIII

FLUORESCENT INDICATORS

Compound	Color change	pH
Methyl-acridone	green—violet	0–1.5
Benzoflavin	yellow—green	0.3–1.7
Aesculin	colorless—blue	1.5–2.0
Ethoxy-acridone	green—violet	1.2–3.2
Salicylic acid	colorless—blue	2.5–3.5
α-Naphthylamine	colorless—blue	3.4–4.8
Acridone	green—violet	4.9–5.1
Quinine	blue—violet	5.9–6.1
Umbelliferone	colorless—blue	6.5–7.6
α-Naphthol sulfonic acid	blue—violet	8–9
β-Naphthol sulfonic acid	blue—violet	9–10
Quinine	violet—colorless	9.5–10
α-Naphthionic acid	blue—green	9–11
β-Naphthionic acid	blue—violet	12–13

Fluorescent indicators may be used exactly like ordinary color indicators for titration with sodium hydroxide, nitric acid, etc. Once more, however, one has to be careful that the fluorescence which should appear at a certain acidity is not quenched by the presence of some quenching agent which is

not connected with the *p*H. of the solution. A very characteristic example of this kind is provided by a dilute solution of quinine sulfate in water. Addition of small quantities of hydrochloric acid of low concentration turns the violet fluorescence of the neutral solution into the light blue color characteristic of acidified solutions. With a little more hydrochloric acid added, the color changes back to violet. The light blue fluorescence of the doubly charged ions is quenched by the presence of Cl^- ions much more than the violet fluorescence of the ions carrying only one positive charge. If a quinine sulfate solution contains some dissociated halogen salts which do not alter the *p*H, and if it is acidified by addition of any acid, the light blue fluorescence does not appear at all.

Insufficient work has been done so far to provide a clear judgment concerning the advantages of fluorescent indicators as compared to ordinary color indicators. It does not seem that fluorescent indicators have already found much application in routine laboratory work. The very small concentration of the fluorescent compounds which is needed is certainly an advantage. Their addition does not change the solution under investigation to any appreciable degree. As a further advantage it is alleged that fluorescent indicators excited by black light can be used for the titration of colored liquids. The color changes of ordinary indicators would be masked completely under these conditions. Thus the titration of red wine or of fruit juice with umbelliferon gives quite satisfactory results. Similar results cannot be achieved with beer because of its own rather strong fluorescence. The same difficulty occurring in all kinds of fluorescence analysis is met with once more. Haitinger proposes that in such cases one should make separate photometric measurements of the fluorescence of the liquid itself and of the indicator added to the liquid. However, this procedure would again render the method very complicated.

7. Technical Identification of Materials

The application of "black light" fluorescence to industrial tests has even a greater scope than fluorescence analysis in scientific research. There is hardly a branch of industry, commerce or other activity in which some sort of material is to be identified, controlled or assorted and for which the use of fluorescence investigation has not at least been recommended. In the books quoted in the bibliography one may find paragraphs on the dyestuff and drug industries, paints, varnishes, paper, cellulose, rubber, tanning and leather, glass and other silicates, pottery, gems, textiles, fuels, tars, soaps and other cosmetics, foodstuffs and food products, with subsections on meat and fish, eggs, wines and fruit juices, beer, vegetables, flour and bakery products, sugar and confectioneries, honey, marmalade, milk and cheese, butter and margarine, and further on mining and prospect-

ing, on silk worms, on philately, museum work, custom examination, forgery and criminology.

The list could probably be still further extended if for conceivable reasons many firms would not withhold their experiences from publication.* On the other hand a perusal of the literature shows that the published results are in many cases rather contradictory. This does not disprove the very manifold uses of the method, but it suggests that a casual remark made by Grant in an article on fluorescence analysis might deserve a far more general application.[21] Grant states that the method is used to best advantage when adapted by each worker to his own requirements. If a difference in the color or the intensity of fluorescence of two materials has been perceived once, it will easily be recognized a second time, while the description of the fluorescence as being greenish brown in one case and olive green or brownish green in another, which might be found in a book, will sometimes not be very helpful. Therefore we shall not endeavor to once more collect as many statements as have been published in the periodicals of all branches of industry and to array them in the order of such branches.† We will rather try to set up the main principles, according to which fluorescence tests may be used in general and to find the limits of each mode of application. Only a few examples shall be mentioned in every case.

The following seem to be the most important and most frequently encountered types of fluorescence tests:

a. Discrimination between different "genuine" materials.‡
b. Determination of the age of a material.
c. Discovery of stains, flaws, etc.
d. Proof of forgery, adulteration or imitation.
e. Artificial fluorescence marks.

In none of these cases are fluorescence tests perfectly unequivocal by themselves, but in almost every case they will give important information by means of an exceedingly simple method.

a. The discrimination between different materials is the domain where a little personal experience is perhaps most important. Not only will almost every white or colorless material like paper, linen, porcelain or glass, coming from different sources and hardly distinguishable in daylight, have very different fluorescence properties, but the same is true for colored materials whose daylight colors seem completely alike. It is utterly improb-

* We happened to learn some 15 years ago that even at this early date the firm of Bayer was secretly using fluorescence tests for discrimination between their "genuine" aspirin and acetylsalicylic tablets manufactured by other chemical works.

† A very complete enumeration of this kind is to be found in the book by Radley and Grant. (See ref. *B* 4 in the bibliography, page ix.)

‡ "Genuine" is used here for materials of somewhat different nature in contradistinction to materials which may be intentionally adulterated or falsified.

able that two samples show the same daylight color and the same fluorescence if they are not really of identical nature.

In the dyestuff[16,60] or drug[61,62] industry, qualitative chemical fluorescence analysis is rather unreliable, as was mentioned in section 3 of this chapter. However, certain products recurring regularly in some kinds of trade are identified without difficulty under "black light," especially if the test is combined with one of the adsorption methods. The same is true for the different natural and synthetic tanning agents,[63] vegetable[64] and mineral oils,[65] butter and margarine,[66] raw and vulcanized rubber,[67] and so on, always under the assumption that no fraud is to be suspected.

The use of fluorescence for the distinction of metal-bearing ore from other minerals in zinc or tungsten mines has already been mentioned.* Fluorescence has proved its value also to the petroleum prospector for the discovery of oil-bearing sands.[68] The assertion that in certain cases even the exact nature of the oil contained in the sand can be recognized from the fluorescence color should certainly not be too greatly generalized.

b. The small concentration of a luminescent compound which is sufficient for the production of a strong luminescence provides in many cases the means of perceiving slight superficial changes of a material due to oxidation or other alteration when aging effects cannot be recognized by other means such as discoloration, odor, etc. This is especially useful for the control of foodstuffs. Fish, hardly fluorescent at all immediately after killing, show a strong violet luminescence after one or two days when kept in a cool room; this is long before the ordinary appearance would prove the fish to be no longer very fresh.† Vegetables which are not fit for preservation because of deterioration are more easily recognized and eliminated with the aid of an "analytic lamp" than by any other method.† The fluorescence of milk and of milk products which have been exposed to daylight turns from yellow into blue after some time because of the conversion of riboflavin into lumichrome. However, in the dark the yellow fluorescence

* See page 100. Willemite and Scheelite do not fluoresce under "black light" excitation. The lamps used for this purpose must emit light of wave-lengths below 3000 Å. † See ref. *B* 1, page ix.

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[60] A. H. Cook, *J. Soc. Chem. Ind.*, **55**, 724 (1936).

[61] P. W. Danckwortt and E. Pfau, *Analyst*. **52**, 707 (1927).

[62] H. Fischer, *Die physikalische Chemie in der gerichtlichen Medizin und in der Toxikologie*. A. Rudolf, Zurich 1925.

[63] O. Gerngross, *Angew. Chem.*, **39**, 696 (1926) and **41**, 50 (1928).

[64] G. Lunde and F. Stiebel, *ibid.*, **46**, 243 (1933).

[65] J. Muir, *Ind. Eng. Chem., Anal. Ed.*, **8**, 432 (1932).

[66] M. Haitinger and H. Joerg and V. Reich, *Angew. Chem.*, **41**, 815 (1928).

[67] F. Kirchhoff, *Kautschuk*, **4**, 24 (1928).

[68] J. Melhase, *Mineral.*, **4**, 9 (1936).

of milk preserved with formaldehyde persists for many months.*[69] The fluorescence of eggs, the white as well as the shells, is also supposed to vary with time,[69] though in this case the method of preservation rather than the pure time factor seems of deciding influence.[70]

The aging of rubber caused by natural or artificial oxidation can be followed by observation of its changing fluorescence.† Only a few examples of this kind, like the differentiation of old and new cotton used for upholstery, have been mentioned so far.[71] It is probable, however, that similar results could be obtained with many materials in which fading or other symptoms of aging are much more difficult to observe.

When the surfaces of marble, ivory, bone or glass are exposed for long periods to the influence of the atmosphere and of daylight, they show a characteristic fluorescence different from that of freshly cut or polished pieces.[72] Even when by an adequate treatment the "patina" seems to be reproduced quite satisfactorily the fluorescence color is a proof of the falsification.

c. Irregularities or flaws which would be quite invisible in daylight appear frequently with great distinctness under black light illumination. In the culling of seed beans the meat of the dried beans shows a bright blue fluorescence under black light illumination while the skin remains practically quite dark. Thus breaks in the skin where the seed beans might be attacked by vermin are much more easily discovered than in daylight.

A damaged object that has been repaired ever so artfully, be it a valuable print or a rare stamp, a vase or a work of sculpture, is recognized by the specific fluorescence of the cemented joints. Restorations of old paintings or of majolica plates will never have the same fluorescence qualities as the original surrounding parts. Other examples of this kind are invisible stains on a paper produced by traces of some glue or even by the mere circumstance that the paper had been in contact with another sheet bearing a cancellation mark,[73] chemical erasures on a document,[74] writing with "secret inks," blemishes on textiles or garments due to oil, mold or some excretion of the human body.

Stains produced by sperma cannot be identified with certainty by their

* The hypothesis advanced by some authors that the yellow fluorescence of milk is connected with its fat content is erroneous. † See ref. *B* 1, page ix.

[69] G. W. Baker, *Analyst*, **57**, 38 (1932).

[70] J. E. H. van Waegeningh and J. E. Heesterman, *Chem. Weekblad*, **29**, 134–138–650 (1932).

[71] A. W. Winne and J. D. Donnovan, *Am. Dyestuff Reptr.*, **21**, 601 (1932).

[72] J. J. Rorimer, *Ultra-violet Rays and Their Use in the Examination of Works of Art.* Metropolitan Museum, New York 1931.

[73] W. H. S. Cheavin and B. D. H. Walter, *The London Philatelist*, **39**, 261 (1930).

[74] C. A. Mitchell, *Analyst*, **58**, 532 (1932).

fluorescence, a test which would be very important for criminology. They are not sufficiently distinct from stains due to perspiration or some other possible origin. The hematoporphyrin fluorescence test for blood stains seems to be the only unequivocal one in this kind of research.[75] But the bare possibility of proving the existence of an otherwise invisible stain by a very simple procedure may be helpful, while the origin of the stain would have to be ascertained by other methods afterwards.

d. Many of the cases mentioned under *b* and *c* are intimately related to the use of fluorescence observations for the detection of imitations, adulterations or forgeries. Such tests have of course a one hundred per cent security only if the forger is not aware of the importance of fluorescence, a possibility which is probably disappearing quickly, or if he is not able to imitate the fluorescence of the original. For the present, at least, "old-age fluorescence" and the flaws on restored works of art seem to belong to the second class. Fluorescence tests may still provide an additional safety for the collector.

If, however, in times past the stamp forger endeavored to copy only the daylight color of some rare specimen without knowing that the original was dyed with rhodamine and should fluoresce with a brilliant red color even in the light of a sodium lamp,* he will be more wary the next time and take as much care with the correct fluorescence as with the correct drawing. This is just one example of many similar cases. In honest trade it will never be doubted whether a bottle contains virgin or refined olive oil. The label will tell. An intended fraud might be detected by the fluorescence of the oil which is orange yellow for the first, blue for the second. The orange fluorescence is due to a content of chlorophyll which is destroyed by the process of distillation. Addition of a small quantity of a chlorophyll solution after the distillation will restore the typical "virgin" fluorescence to the refined oil. The forewarned forger will certainly be able to execute this easy operation but he will probably have to take greater pains to eliminate the strong blue fluorescence due to an addition of mineral oils to a vegetable oil destined for the manufacture of a cosmetic lotion.

The manufacture of fluorescent false teeth may be called a very harmless kind of forgery. The brilliant whitish fluorescence of natural teeth under black light illumination is, according to Tiede, due to the collagen content of the calcium phosphate of which they consist. An artificial tooth made of porcelain appears as a black hole in the shining row under these conditions.

* Rhodamines are the only synthetic red dyestuffs which show a red fluorescence when irradiated with the light of a sodium lamp.

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[75] Ch. Dhéré, *La Fluorescence en Biochimie*, Masson, Paris 1934; H. Fischer, *Die physikalische Chemie in der gerichtlichen Medizin und in der Toxikologie*, A. Rudolf, Zurich 1925.

The new flubrescent variety is made of a plastic containing traces of a fluorescent compound. Since the fluorescence of teeth is quite invisible in a normally lighted room, even if mercury lamps are used for the production of light, the new invention should be interesting only for persons who have to exhibit themselves under black light illumination.

There are cases where a fluorescence test is perfectly safe for the discrimination between an imitation and the genuine article, but where simpler methods of distinction make the fluorescence test superfluous. The red fluorescence of a real ruby will be wanting in the best glass imitations, but no jeweler needs black light to make sure of the counterfeit. On the other hand the fluorescence spectra of synthetic ruby and of the natural gem are identical and offer no means of discrimination.*[76] However, according to Tiede, the synthetic products show an easily perceivable afterglow missing in the case of the natural gems and this might provide a means of distinguishing one from the other.[77]

Taking everything into account, it may be said that though fluorescence tests give in general no absolute security, they have become a very valuable help against all kinds of frauds.

e. So far only the natural proper fluorescence of different materials has been taken into account. It is, of course, possible to mark a material by addition of a small quantity of an invisible and otherwise harmless fluorescing compound, so that in black light it becomes distinguishable from similar material not marked in the same way. Though it seems to be certain that a good many manufacturers are using the method, not much detail is known about it. A special application of the principle is the use of invisible fluorescing "watermarks" on bank notes, check forms or other papers destined for important documents. This again is no absolute protection against forgery, but it is another way to render the forger's art more difficult.[78]

The natural bluish fluorescence of lubricating oils for motor cars is frequently increased by addition of some hydrocarbons. This is probably done rather for beauty's sake than for protection against imitation.

Finally we mention occasions where invisible fluorescent marks are even

* This was proved by numerous spectrograms published by different authors. It is therefore not clear why, according to Radley's and Grant's own experience, the fluorescence color of natural rubies should always be much less deeply red than that of synthetic stones. Concerning the difference between the fluorescence of Ceylon rubies and those of other origin, see page 98.

[76] R. W. Wood and C. E. Mendenhall, *Phil. Mag.*, **30**, 316 (1915); H. Dubois and G. J. Elias, *Ann. Physik*, **27**, 233 (1908) and **35**, 617 (1941); H. C. Dake and J. A. De Ment, *Fluorescent Light and Its Applications*, Chemical Publ. Co., Brooklyn 1941.

[77] E. Tiede and A. Chomse, *Chem. Ber.*, **67**, 1988 (1934).

[78] J. Grant, *Analyst*, **58**, 603 (1933).

used for the discrimination between different categories of human beings. Newborn babies in a nursery may thus be protected from being exchanged. Dance hall managers may be protected from being cheated by guests who have not paid their admission fee. Dyes in very dilute shellac solutions are used on a stamp pad and the patron is stamped on the wrist in a "check-out" tag.

8. Use of Fluorescence Microscope

If very small objects or mixtures of very minute particles have to be investigated, the fluorescence microscope can be helpful for analysis. The proper fluorescence of the material or more frequently the induced fluorescence obtained by "fluorochromy" are employed.

In powders, single grains of another nature can be perceived, *e.g.*, crystals of mercuric chloride appear dark in a strongly fluorescent powder of calomel and cocoa husk differs in its fluorescence from ground cocoa, the same being true for fraudulent admixtures to flour or spices. The cathode ray fluorescence microscope described on page 67, was devised for the purpose of picking the grains with the strongest luminescence out of a microcrystalline powder of zinc silicate.

The possibility of identifying certain bacteria under the fluorescence microscope is rapidly gaining importance. The method is already used extensively for the tuberculosis test in sputum or body fluids.[79] Instead of confining the observation to the proper fluorescence of the bacilli, these are stained with auramine O as fluorochrome.* The dyestuff is retained by the bacteria, when the surrounding material is de-stained by means of acidified alcohol. The exciting light is filtered through a blue ultraviolet transmitting glass and the bright fluorescence is observed through a yellow filter. As the fluorescent bacteria are seen on an almost completely dark background (Fig. 48b), less magnification is required and a larger field of vision is provided. Thus the test becomes more sensitive than the older method and reduces the time for identification by about one-third.

In the same way fluorescence microscopy has been applied to the analysis of leprosy bacteria, trypanosomes and spirochetes and the diphtheria organism.[79] Some authors claim even to have demonstrated a virus stained with primulin under the fluorescence microscope,[80] but the validity of this assertion has been questioned by others.

In dermatologic practice, fluorescence microscopy helps detect pathological conditions of the skin and to differentiate fungi in cultures. In-

* The proper fluorescence of the bacteria due to their porphyrin content, mentioned on page 103, is much weaker and therefore not suitable for a rapid examination.

[79] O. W. Richards and D. K. Miller, *Am. J. Clin. Path.*, **11**, techn. suppl. 5, 1 (1941); O. W. Richards, F. K. Kline and R. E. Leach, *Am. Rev. Tuberculosis*, **46**, 255 (1941).

[80] F. Gerlach, *Wien. klin. Wochschr.*, No. 46, 50 (1937).

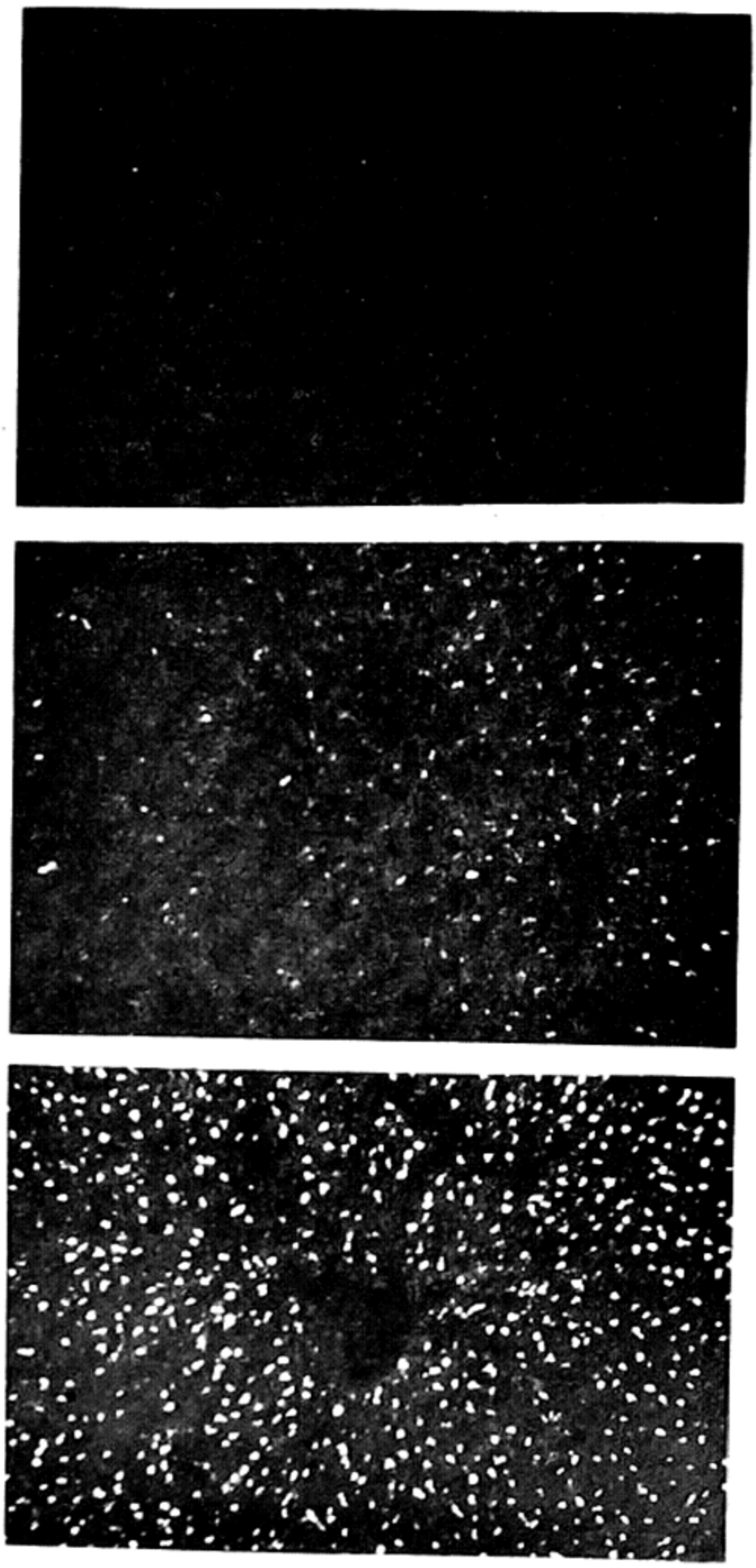


Fig. 48a.—Fluorescence of vitamin A under fluorescence microscope (Popper).

a: Liver of rat deficient in vitamin A. b: Normal liver with moderate vitamin A fluorescence. c: Liver of rat made hypervitaminotic with vitamin A (from *Arch. Path.*, **72,** 11 (1941).

fection of skin or hair by some kind of fungi can frequently be recognized by its fluorescence without the use of a microscope.[81]

[81] G. M. Lewis and M. E. Hopper, *Introduction to Medical Mycology*, Year Book Publishers, Chicago 1939; pp. 233–238.

The main purpose of fluorescence microscopy, as of ordinary microscopy, is observation of small objects and of their structure rather than mere identification or analysis. On a non-luminescent or differently luminescent background the proper fluorescence of certain parts of plants or animal tissues occasionally reveals details which are not perceived as easily under

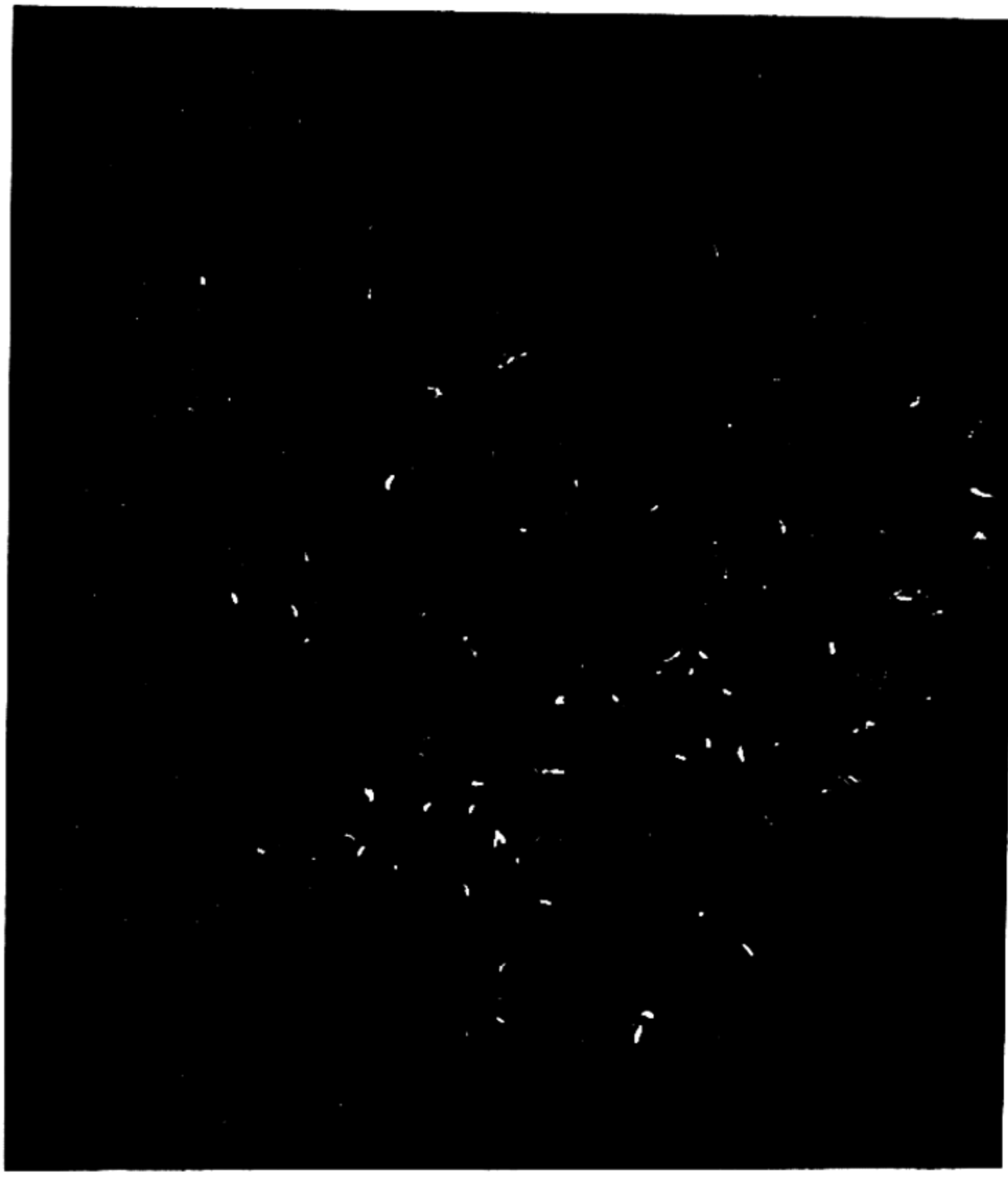


Fig. 48b.—Fluorescent tuberculosis bacteria. (Courtesy of Spencer Lens Co.)

white light illumination. According to H. Popper cytoplasms in an animal organ appear a faint blue, the collagenous fibres a striking blue, and the elastic fibres a brilliant gray. The orientation in an unstained section under the fluorescence microscope is as easy as in a stained section with visible light.[82]

By means of the "fading green fluorescence" which is due to the presence

[82] H. Popper, *Arch. Path.*, **31**, 766 (1941).

of lipoids carrying vitamin A* the distribution of this vitamin in various normal and pathological organs has been studied in photomicrographs (Fig. 48a). The material is fixed in formalin and water serves as mounting medium. Exposures of less than 30 seconds are sufficient, longer exposures being disadvantageous because of the fading nature of the fluorescence. During the first half minute, the vitamin A fluorescence is so strong that it is clearly recognized even if the lipoids carrying the vitamin are simultaneously rendered visible in the micrograph by "fluorochromy," using phosphine 3R.

The method of fluorochromy is particularly favorable if adjacent parts of a material acquire contrasting fluorescence colors by adsorption of the same dyestuff or if they adsorb preferentially different dyes. If the tissue of a human palate is stained with choriphosphine, the fluorescence colors are orange red for the phlegm, greenish yellow for the cellular nuclei; light yellow for the plasma, olive green for the muscular fibres, and bluish green for the fatty substance. An example of the simultaneous use of several fluorochromes ("polyfluorochromy") is provided by the cross-section of a plant seed. Aminoterephthalic acid imparts a light blue fluorescence to the protein crystals, the cellulose adsorbs primulin, and the oil droplets dissolve chlorophyll and fluoresce in a bright yellow and red color respectively. These two examples are taken from Haitinger's monograph on fluorescence microscopy, where a good many more of a similar kind may be found. How far and to what advantage the method has already been used, not for the demonstration of its possibility but for research work, is another question.

Because of the small dyestuff concentration sufficient to produce fluorescence, fluorochromy can even be applied to the microscopic observation of living organisms like the liver or the kidney of a frog. Fluorescein, trypaflavine and primulin have proved best adapted for this purpose. Staining these organisms with ordinary non-fluorescent dyes would be equivalent to poisoning.

The observation of living bacteria under the fluorescence microscope by means of their proper fluorescence even without the use of fluorochromy is sometimes superior to ordinary microscopy.

9. Tracing of Hidden Currents

The tracing of a subterraneous connection between different waterways was one of the earliest attempts to apply the strong photoluminescence of fluorescein even at highest dilution to a practical purpose. According to the Athenaeum of 1878, ten liters of a concentrated uranin solution were poured into the bed of the upper current of the Danube which in dry summers is completely sucked up by the porous lime rocks of the Jura mountains.

* See page 104.

Fifty hours later the fluorescence could be observed in the water of the river Aache which springs from the same mountains many miles to the south and flows into the Bodensee. Thus the existence of a connection between the river systems of the Rhine and the Danube was demonstrated.

On a much smaller scale, experiments of the same kind were performed at the beginning of this century and later in order to locate the transportation of matter through the human body. Fluorescein was either injected into the veins or administered orally in quantities up to several grams and the presence or absence of the fluorescence in blood extracted from different parts of the body, in urine, bile, saliva, etc., was used as a proof that within a certain time the dyestuff had been carried along to a certain point.[83]

These early experiments showed that a connection existed between two points, without providing any knowledge concerning the way by which the connection was effectuated. By the improved modern methods of excitation by means of black light, it became possible to excite and perceive the fluorescence of uranin through the skin within the living tissue. A few cc. of a 5% aqueous uranin solution are injected intravenously. After the circulation time has passed, the part under observation (lips, tongue, eyelids) suddenly acquires a greenish yellow appearance. The end point is so sharply defined that it supplies the first easy objective method to determine the circulation time in normal persons and in patients suffering from a heart disease. For this test the solution is injected into the arm and the time elapsing before the fluorescence shows up in the lip is measured.

Since the fluorescein is carried along with the blood, no fluorescence appears in tissues or organs in which the blood circulation is hindered. This may become a very important aid, for the diagnosis of peripheral vascular disease like diabetic gangrene, as well as in certain surgical operations.[84]

In contradistinction to eosin and the other halide substituted derivatives, fluorescein is supposed to be non-toxic. It is rapidly excreted into the urine, and with normal renal function the fluorescence is no longer visible in the plasma after five hours have elapsed. Nevertheless, the new method, which is very promising and only in its first stage of development, should not be applied without certain precautions as far as experiments with human patients are concerned. After an injection the whole skin becomes more or less fluorescent; the dyestuff, however, is not only luminescent after absorption of light but it is also a photosensitizer. Thus without being harmful in the dark, it might well become detrimental when strongly irradiated. Cases of hemolysis by fluorescent dyestuffs are well known. Diseases produced in domestic animals by light sensitivity are now con-

[83] K. Wessely, *Arch. ges. Physiol.*, *1908*, p. 548; H. Strauss, *Berlin klin. Wochschr.*, **50**, 2226 (1913); E. Koch, *Deut. Arch. klin. Med.*, **140**, 39 (1922).

[84] K. Lange and L. J. Boyd, *Med. Clinics of N. America*, **1942**, p. 943; J. Herrlin, S. Th. Glasser, and K. Lange, *Arch. Surg.*, **45**, 785 (1942).

sidered to be not infrequent, and this light sensitivity is acquired by grazing on certain weeds, which contain fluorescent and sensitizing dyestuffs, such as hypericin in the weed called St. Johnswort.[85] *In vitro*, hemolysis has also been produced under sunlight illumination using fluorescein as a sensitizer. It is a fortunate, though not fortuitous, coincidence that the dyestuffs with the highest fluorescence yield are relatively bad sensitizers—fluorescein, for instance, as compared with erythrosin or rose bengale. (See Chapter II, Table IV.) Thus a weak and short irradiation of the fluorescent dye within the human body which must be applied for the medical observation is probably quite innocuous. However, it is advisable to keep the patient, after a fluorescein treatment, in a room which is not too strongly illuminated, until most of the dye has been excreted and the skin is no longer fluorescent.

Plant physiology has also made use of fluorescent dyes for studying the transportation of matter inside of a living plant. If a leaf is slightly scratched and a solution of fluorescein or aesculin in water or gelatin is applied to this spot, the dye enters the leaf which at once begins to show, under black light illumination, the typical blue or green dyestuff fluorescence. In a water-deficient plant the water is absorbed greedily and flows downward through the xylem carrying the fluorescent dye along. In this case it is not even stopped when it has to pass a scalded region. In a well-watered plant, however, the dye travels exclusively through the sieve tubes (the phloem) and reaches the stem through the petiole, if it is not stopped on its way by a scalded region of the leaf. The velocity of the transport can be easily followed by observing the distance to which the fluorescence has been carried in a given time; this velocity can be as high as 0.5 cm. per minute, much higher than the diffusion velocity of the dye molecules in water, but it depends to a great degree on the temperature. The details of these phenomena must be studied under a fluorescent microscope.[86]

It is of course important to choose for such experiments plants which have no fluorescence emission of their own in the same spectral region as the dyestuffs. If the xylem of woody plants becomes fluorescent after exposure to ammonia vapor, this cannot be ascribed to the fluorescein, which may be present in the xylem and whose fluorescence was suppressed by the acidity of the plant sap. Many woody plants, showing no or only very weak fluorescence under normal conditions, become brilliantly fluorescent after exposure to ammonia vapor and the color of the fluorescence is very similar to that of fluorescein, though the plant has never been contaminated with any foreign dye.

[85] H. F. Blum, *Photodynamic Action and Diseases Caused by Light*, Am. Chem. Soc. Monogr. Series, Reinhold, New York 1941.

[86] W. Schumacher, *Jahrb. wiss. Botan.*, **77**, 685 (1933); E. M. Palmquist, *Am. J. Botany*, **26**, 655 (1939).

CHAPTER VI

LUMINESCENCE AS A LIGHT SOURCE

1. Luminescent Paints

Three types of luminescent paints are available for technical application; fluorescent, phosphorescent and self-luminous. Each of these will be treated separately in the following paragraphs.

Frequently the surface of a material can be made luminous without the use of a paint either by incorporating a luminescent compound directly in a plastic or by dyeing a textile, a paper, etc., by absorption of a fluorescent solution.

Although luminescent material has in the past five years exhibited an enormous development, it seems to be yet in its infancy. Attempts have been made to standardize the products as to their luminosity, but so far they have met with no definite results.

a. Fluorescent Paints

The usual method for the production of fluorescent paints is to incorporate a fluorescent organic compound in a vehicle either of a lacquer or of an oil base. The vehicle must be such that it does not react with the fluorescent compound, even under the action of the exciting light.[1] Each fluorescent substance has an optimum concentration and a *p*H value for maximum efficiency in a liquid solution. They must, however, be determined experimentally so that not the liquid solution but the dried solid film after the application of the paint responds with maximum efficiency. In general the fluorescence of the dried film is much more brilliant than that of the liquid paint.

If a transparent vehicle is used the choice of undercoat must be carefully considered: it must be a white paint with a high reflecting power for the near U.V. Paints of this nature were investigated by Luckiesh and Holladay,[2] who found that a large proportion of MgO, MgB_2O_3 and Al_2O_3 gives the best results. For most purposes, however, a cheaper mixture of zinc white (ZnO) and titanium oxide (TiO_2) suffices. Nitrocellulose lacquers are the most advantageous transparent vehicles. Non-transparent paints are prepared by pigmenting the lacquer with finely ground ZnS.* Fluo-

* BaS, which is frequently recommended, is not so advantageous.

[1] A. Strobel and R. L. Zahour, *Trans. Illum. Eng. Soc.*, **28**, 612 (1933); O. Petzold and V. Demant, *Paint Manuf.*, **10**, 174 and 186 (1940).

[2] M. Luckiesh and L. L. Holladay, *J. Franklin Inst.*, **212**, 787 (1931).

rescent paints are applied to the desired surface like any other paint. When dried they must be protected by a coat of clear lacquer.*

Table XIV lists a series of dyestuffs, of dyestuff mixtures[3] and of aromatic hydrocarbons which are especially useful for the manufacture of fluorescent lacquers.† The concentration is in all cases of the order of 1.5 g. dyestuff per kg. lacquer. Substances like anthracene or chrysene are not sufficiently soluble and must be ground into the varnish. Crude commercial anthracene, contaminated with naphthacene, produces a lacquer with a brilliant green fluorescence. From a mixture of pure anthracene and rhodamine B extra, a pink fluorescing paint is obtained; the fluorescence of a well-balanced combination of rhodamine, auramine and primulin is nearly pure white.

Frequently the fluorescence color of organic dye paints coincides closely with their daylight body color and this may in certain cases have some advantage.[4] It is a consequence of the validity of Stokes' law. The wave-length of the fluorescence band is somewhat greater than the wave-length of the absorption band, and the light transmitted through the dye and thus defining its color has also wave-lengths different and frequently longer than those of the absorption band. With the peak of the absorption in the blue, fluorescence and body color are green. Rhodamine B extra, which is a red dye, shows a red fluorescence. This rule, however, is by no means a strict one: the fluorescence of eosin, which is also a red dye, is greenish yellow.

TABLE XIV

FLUORESCENT LACQUERS

Color of fluorescence	Fluorescent compound
Red	Rhodamine B extra
Orange	Rhodamine B extra + auramine base
Yellow	Rhodamine 6G extra + auramine base
Greenish yellow—yellowish green*	Auramine + primulin
Green—green blue	Thioflavin S + primulin
Blue	Carbazol, chrysene, or anthranilic acid
Blue violet	Anthracene

* According to the relative quantity of the two components.

* This lacquer, as well as the vehicle in which the fluorescent compound is imbedded, must be transparent to the exciting ultraviolet light and must not be discolored by sunlight.

† A great many other dyestuffs are serviceable for the purpose.

[3] J. N. Bowtell, W. E. Harper, and M. B. Robinson, *Trans. Illum. Eng. Soc.*, **5**, 57 (1940).

[4] G. F. A. Stutz, *J. Optical Soc. Am.*, **32**, 626 (1942).

Rhodamine dyes dissolved in cellulose nitrate or acetate or in a molten alkyd resin like paralac produce beautifully fluorescent plastic sheeting from which fancy designs can be cut.[5]

Cloth material is made fluorescent by dipping it into a liquid solution containing from 0.5 to 1% of a fluorescing compound. Here again the rhodamines are brilliantly fluorescent in almost every case, when dyed on natural and artificial silk, on wool, or on cotton, as long as these are not treated with a tannin mordant. But for one and the same dye the hue of the fluorescence color frequently varies rather widely according to the Nature of the cloth.[6] The fluorescence of rhodamine 6G is pinkish yellow on cotton, yellowish gold on silk, red gold on wool, wine red on unbleached sulfite pulp, and yellow green on bleached pulp. Other dyestuffs behave similarly. In some cases the shade is further altered by an additional fluorescence of the cloth itself: wool has often a strong bluish fluorescence of its own. Some dyestuffs are strongly fluorescent when applied to silk or viscose rayon and very little or not at all on wool or cotton.[6a]

Fluorescent writing inks are manufactured, in the same way as other inks, by dissolving a fluorescent compound like rhodamine for red fluorescence or quinine sulfate for blue fluorescence in water. Fluorescent inks can be used for printing in the same way as ordinary printing inks. Such inks are prepared either by precipitating a fluorescent dyestuff on $Al(OH)_3$, which is then ground into a varnish, or by grinding the insoluble fluorescent compound itself into the varnish. Sometimes the simplest method for the production of a fluorescent dial is to draw the scale or the lettering on a paper sheet with fluorescent ink and to transfer the drawing to the dial by means of decalcomania.*

Organic fluorescent paints should not be exposed too much to daylight since they are all more or less unstable and inclined to fading with subsequent loss of their luminescence power. The fading is also largely influenced by the vehicle in which the dyestuff is imbedded; it is much slower in cellulose acetate than in glyptal, for instance.[6b] The light-fastness is somewhat improved, if the dyes are applied to an inorganic base to form a lake pigment. The problem of light-fastness is of comparatively less importance if the fluorescent objects are kept in dark rooms, as is very often the case.

If, on the other hand, a fluorescent surface must be continuously exposed to daylight (as for instance the dials of an airplane), it is better to employ paints which are made from inorganic material by grinding finely powdered calcium tungstate, fluorite, zinc sulfide, etc. into some varnish. Such

* Occasionally the silk screen process is used for the printing with fluorescent inks, see page 137.

[5] V. E. Yarsley, *Electrician*, August 8, 1942; *Nature*, **198**, 311 (1940).

[6a] J. Grant, *Textile Colorist*, **62**, 9 (1940).

[6b] G. R. Fonda, *J. Optical Soc. Am.*, **26**, 316 (1936).

paints are to a much higher degree light-fast and weather resistant. It is true that their intrinsic brightness is relatively small. While, according to the intensity of the primary source of radiation, the brightness of dyestuff fluorescent paints may vary between 500 and 3000 microlamberts, the brightness of the inorganic paints will, under the same conditions, not exceed 5–40 microlamberts. This is, however, no serious drawback, if a fluorescent dial is used only in complete darkness with well-adapted eyes.[4]

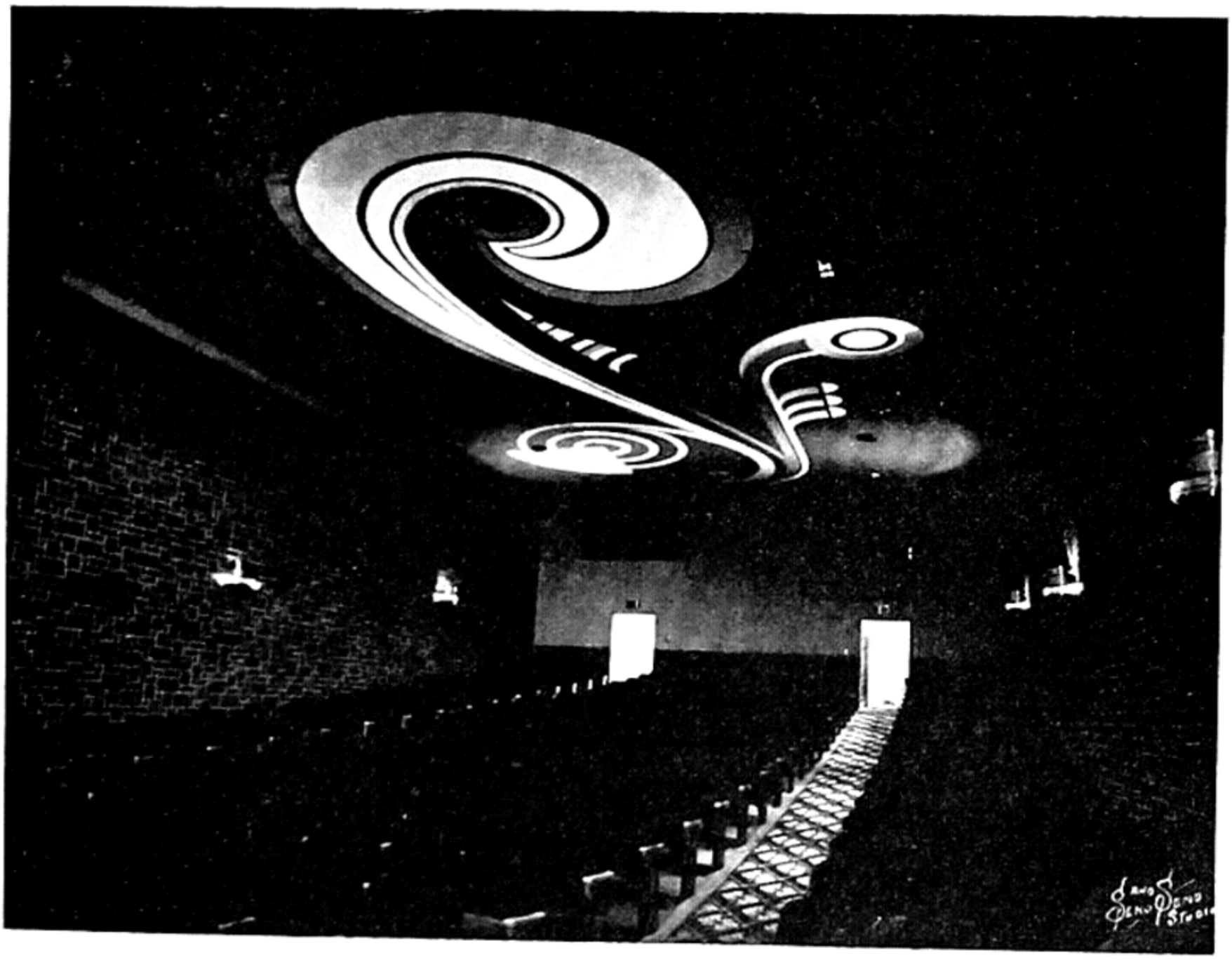


Fig. 49.—Fluorescent carpet and ceiling. (Courtesy of Continental Lithograph Corporation, Cleveland, Ohio.)

Zinc borate activated with manganese and baked at 850° C. produces a fluorescent glaze which is occasionally applied to pottery.[7]

All fluorescent display is necessarily effective only in low overall illumination and under excitation by strong black light which means that the location must be expressly prepared for the purpose. Where the overall illumination is quite low the luminescent surfaces themselves may serve as the source of illumination. Thus theaters, night clubs and bars are fitted with fluorescent carpets or their walls are decorated with murals painted with fluorescent paints (Fig. 49). It is possible in this way to

[7] W. H. Kohl, *Can. J. Research*, **13 A**, 126 (1935).

show very brilliant colors in rooms which are almost completely dark. Similar effects are produced on theater stages using fluorescent cloth for costumes, fluorescent paints for the setting, or even fluorescent make-up (Fig. 50).

Besides these merely decorative purposes, fluorescent paints have found many applications of a really important practical nature.[8] In the dark, for instance, in hospitals and workshops during blackouts, and in theaters during performances, they make visible certain important points like doors,

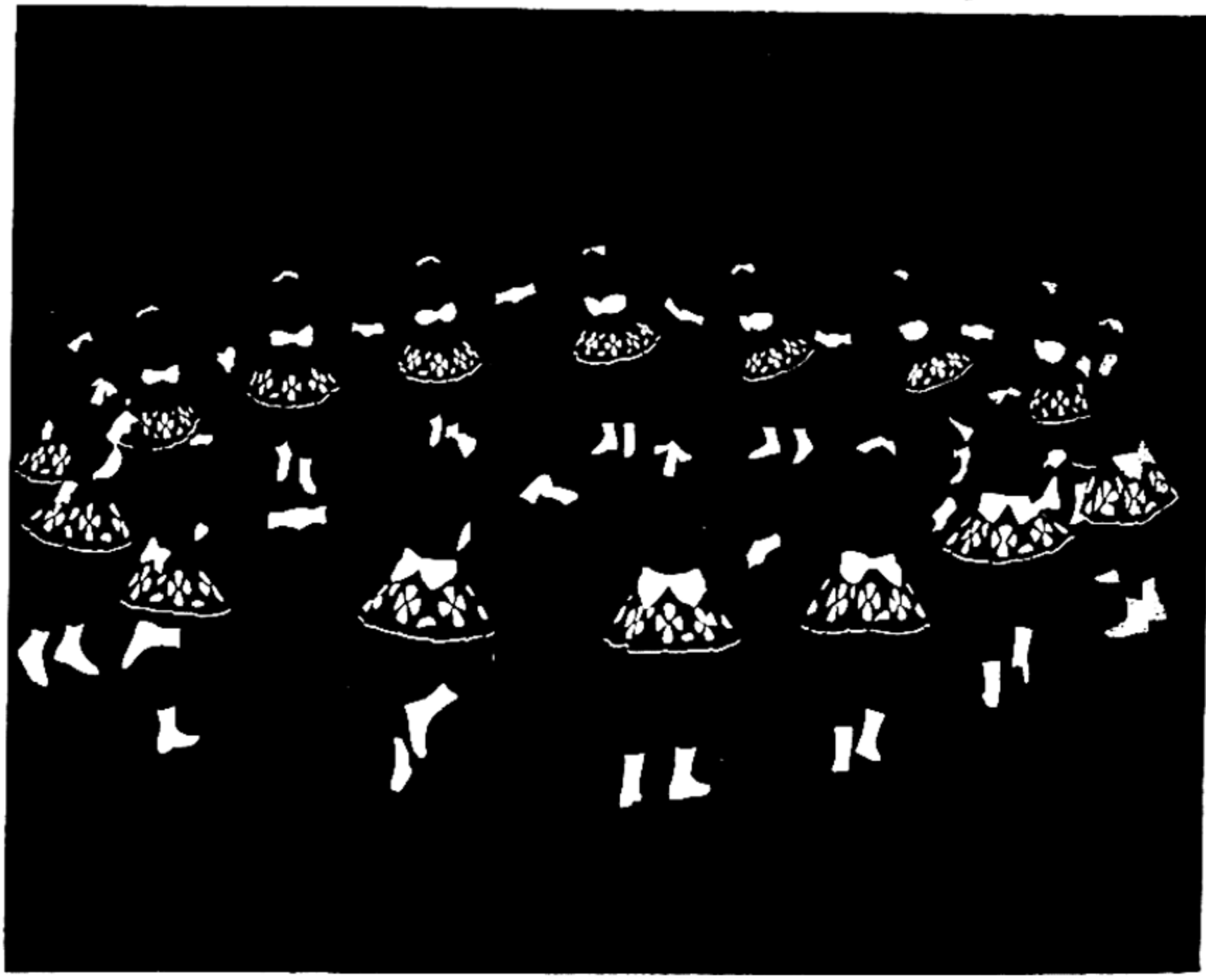


Fig. 50.—Fluorescent ballet. (Courtesy of Continental Lithograph Corporation, Cleveland, Ohio.)

steps and dangerous corners or parts of machinery, without spreading light to other parts of the room. Switchboards of airplanes are equipped with small black light lamps irradiating the fluorescent dials of the different instruments to render possible control at night (Fig. 51). Military maps can be read in the dark when printed or sketched on fluorescent paper.

The peculiarity of some rhodamine paints, the red fluorescence of which is excited even by yellow light, would be of great value for sign posts on high-

[8] R. N. Finch, *Electrical Rev.*, **125**, 258 (1939); N. Riehl and E. A. Fick, *ibid.*, **126**, 461 (1940); L. J. Davies, *Trans. Faraday Soc.*, **35**, 171 (1939).

ways illuminated with sodium lamps for they would appear red just as the motorists are used to see them in daylight instead of dark gray, as they seem now because of the lack of red in the emission spectrum of the sodium arc. But even rhodamine 3B, though it is more stable than most of the other rhodamines, would fade within a few days when continuously exposed to sunlight.[9]

Lipsticks and make-up stained with rhodamine have been patented by several manufacturers. They are able to produce the "natural" color on

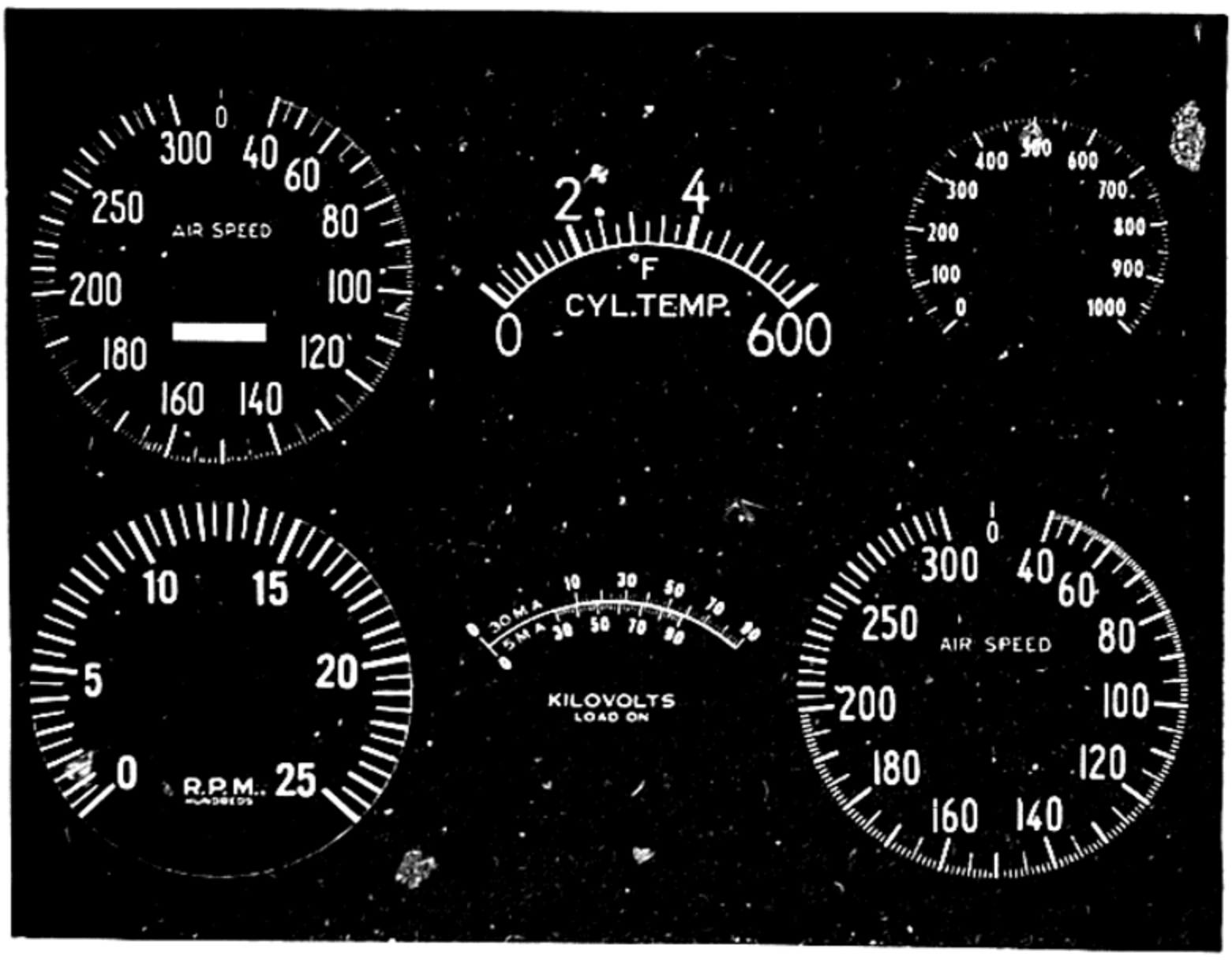


Fig. 51.—Switchboard with fluorescent dials. (Courtesy of Continental Lithograph Corporation, Cleveland, Ohio.)

the lips and cheeks under the ghastly yellow or blue-violet light of sodium or mercury lamps.*

b. Phosphorescent Paints

Phosphors to be employed for the preparation of phosphorescent paints should have a long-lasting afterglow and should be excited by daylight

* Other manufacturers of cosmetics advertise fluorescent anti-sunburn oils or ointments. The fluorescence of such products proves that the harmful ultraviolet radiation of the sun is absorbed at least partially. In itself the fluorescence is harmless, but it contributes nothing to the effectiveness of the stuff.[10]

[9] G. R. Fonda, *J. Optical Soc. Am.*, **26**, 316 (1936).
[10] J. H. Frydlander, *Chem. Zentr.*, **1938, II**, p. 1143.

or better by the radiation of normal electric lamps, which are very poor in ultraviolet and even in violet light. Thus alkaline earth sulfide and zinc sulfide phosphors are used almost exclusively, the first if long duration of the afterglow is desired, the second if high initial intensity is more important. The time needed for full excitation will in general be negligible. With a 500 watt tungsten filament lamp as light source 100 foot-candles suffice to saturate a calcium sulfide phosphor in one minute, a zinc sulfide phosphor even in 15 seconds.[11] The formulation, manufacture and application of phosphorescent paints need a great deal of experience. This is especially true with regard to the selection of a vehicle for the paint.

The usual type of a paint vehicle, a raw or processed linseed or wood oil, or a varnish made with these oils, cannot be used in phosphorescent paints. Such vehicles react with the phosphors causing livering, evolution of H_2S, and subsequent vanishing of the luminescence. Refined perilla oils appear to mix without trouble but in general the paint formulator is restricted to work with non-oxidizing vehicles such as solutions of natural or synthetic resins. Even these have a tendency to react with the sulphides and in order to prevent this J. Nussbaum recommends the addition of 0.01 to 1% of an oxide or nitrate of Zn, Cd or Mg or a sulphuric or sulphamide derivative of an aromatic hydrocarbon. Resistance to moisture is obtained by the addition of 0.1 to 5% of waxes, paraffins, cetyl palmitates, etc. Special care must be taken to keep the acid number of the resin solution as low as possible or at least to obtain a very low water tolerance. The acid value of the resins may be reduced by adding a few per cent of ZnO, MgO or sodium silicate.

Damar varnish has been used a good deal and is still in use in some commercially produced paints. The solvent retention, however, of damar gum and its tendency to resoften in warm weather is rather unsatisfactory. The vinyl resins may be employed successfully although new problems are introduced by the rather powerful solvents needed for their solution and by the peculiar viscosity and the drying characteristics of this group. The coumarone-indene resins, quite serviceable in other respects, are inclined to yellow after some time. The best results are obtained with polystyrene and with polymerized esters of methyl and ethyl methacrylide which appear to be free from all the defects mentioned. Chlorinated rubber (Thornesite) has also been used in luminous paint formulation.[12, 13]

The usual solvents are low boiling hydrocarbons like toluene or xylene if the paint is to be sprayed, or higher boiling compounds like butyl acetate or cellosolve if it is to be brushed.

[11] A. H. Taylor, *J. Optical Soc. Am.*, **32**, 506 (1942).

[12] V. Demant and O. Petzold, *Oil and Colour Trades J.*, **1939**, 95 and 1279; H. C. Bryson, *Paint Ind. Mag.*, **1940**, 86 and 119; H. Hadert, *Farben-Chem.*, **10**, 390 (1939).

[13] C. E. Barnett, *Ind. Eng. Chem., News Ed.*, **20**, 1006 (1942).

One gallon of finished paint contains about 5 pounds of phosphorescent material and 5 pounds of resin dissolved in xylene, toluene, etc. In order to obtain flexible films, an addition of a plasticizer is often necessary. Dibutyl phthalate, which is sometimes recommended, is not very satisfactory and chlorinated diphenyl ("Arochlor"), triethanol amine or castor oil is to be preferred.

The problem of the paint formulator does not end with the selection of the vehicle. Too fine grinding of the phosphor decreases the luminous efficiency. Contrary to standard paint practice, which is to get the pigment ground as finely as possible, luminous paints should be reduced to grains of not less than about 0.1 mm. diameter, corresponding to "200 mesh."[5, 12] This renders the suspension of the phosphorescent powder in the solution somewhat difficult. The addition of suspending agents like bentonite, aluminum stearate or diatomaceous earth might prevent the dry caking of the phosphor in the container upon standing, but is frequently more detrimental than helpful because it may gel the whole solution.

The surface to which the finished paint is to be applied, be it wood, metal, glass or plastic, should first be "primed" with a sealer of clear lacquer or a flat white coat, free from lead, antimony or nickel. Pure TiO_2 or ZnO in boiled perilla oil form a good undercoat. The luminescent paint itself is either sprayed or applied in thin successive coats by means of a brush until an even surface is produced.* One gallon of paint is sufficient to cover from 250 to 400 square feet.[13]

A transparent overcoat must always be applied as soon as the surface is dry in order to protect the phosphor from the oxidizing action of the atmosphere and from moisture. As the luminescent material is composed of relatively large particles, the protective layer is easily eroded and must be frequently renewed.[13, 14]

Because of the coarseness of the grains, ordinary printing with phosphorescent inks is not possible. If mechanical reproduction of pictures or writing with phosphorescent paints is desired, it can be done only by the silk screen process.†[15] CaS or ZnS phosphors incorporated in urea for-

* Small traces of water in the vehicle cause it to gel, choking the nozzle of the spray or gumming up the brush so that the material is no longer useful.

† The silk screen process, which in certain cases is also used for non-phosphorescent paints, is a modification of the well-known method of reproducing a design by means of a stencil. The whole surface of a well-stretched silk screen is covered with a varnish, leaving free only those parts which are to be printed. The paint is applied to the varnished side of the screen under some pressure by a squeegee. Only the unvarnished parts of the silk are pervious to the paint, and so the desired design is printed on a paper or other surface in contact with the reverse side of the screen.

[14] L. Vanino and S. Rothschild, *Chem. Ztg.*, **55**, 477 and 498 (1931); F. Felix, *Faerber Ztg.*, **45**, 519 (1940).

[15] S. Rafaele, *Silk Rayon World J.*, **16**, 14 and 40 (1939).

maldehyde baking enamel* and baked at 200° C. for one hour or at 250° C. for 15 minutes, according to the type of vehicle, produce phosphorescent films on metal or on cloth which are much less easily damaged by moisture, by bending and twisting, etc., than are the usual lacquers. Phosphorescent porcelain or pottery glazes have been formulated in which the phosphors, usually ZnS phosphors, are imbedded. The glaze is fired at a temperature of from 300 to 400° C.

Phosphorescent paints do not require a continuous irradiation. Once excited they remain luminous for several hours. As mentioned in Chapter IV the phosphorescence of zinc and cadmium sulfide phosphors is brighter but less persistent than that of calcium and strontium sulfide phosphors. The useful afterglow of the former is only of the order of one hour or less, while the alkaline earth phosphors remain easily visible during periods from 3 to 10 hours. One hour after the end of the activation the brightness of the best materials has decayed to a microlambert; 0.01 microlambert is about the lowest limit for usefulness. The choice of the most favorable phosphor depends of course on the special purpose for which it is wanted.[5] Two kinds of application are made possible which are not available for fluorescent paints. After the extinction of the normal illumination of a room objects covered with a phosphorescent paint are still visible. And such objects also remain visible when they are removed from an illuminated area out into obscurity.

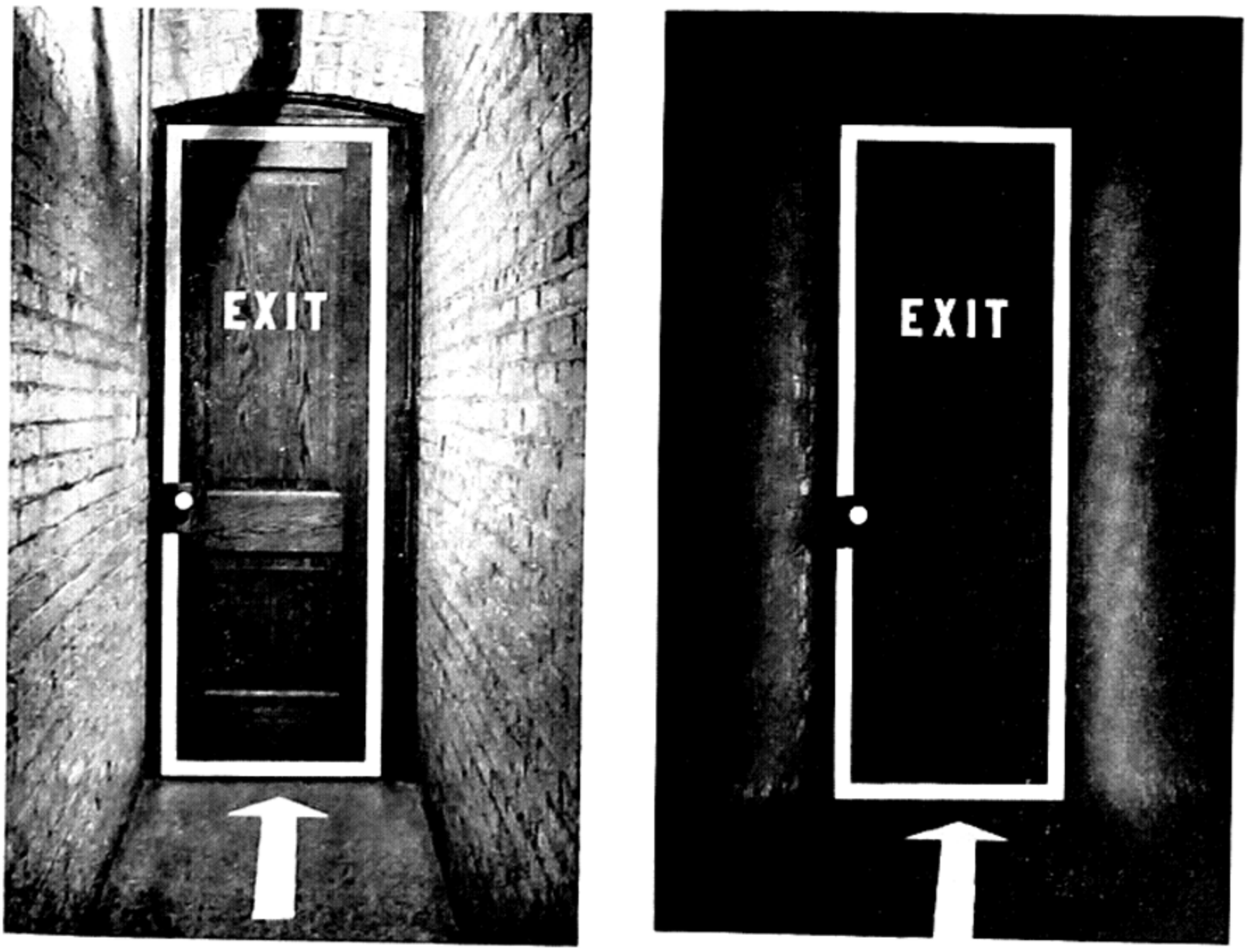
The first of these possibilities is used for emergencies, when for some reason the normal electric supply is cut off, during blackouts indoors as well as on the streets of a town, or in photographic dark rooms, so that certain objects, door frames or door handles, curbstones, or signs indicating entrances or exits may be perceived without difficulty (Fig. 52). A more perfunctory application of the same kind consists in the decoration of wallpapers, lampshades, or other room furnishings, with phosphorescent designs which, after the light is switched off, remain luminous with a soft slowly decaying radiation.

Making use of the second possibility, phosphorescent buttons or studs are taken out into the dark from an illuminated room where they have been excited. Such buttons were in general use in all belligerent countries to protect pedestrians from dangerous collisions on blacked-out streets. According to English government regulations, the brightness of the luminescent paints used for these purposes must be not less than 0.1 equivalent foot-candles during the irradiation by a standard light source. One minute after extinction of the light source, the phosphorescence brightness must be at least 0.005 equivalent foot-candles and must not fall below 0.001

* This material is very generally used as enamel for venetian blinds.

equivalent foot-candles before the end of the period to be stated by the manufacturer.

In general, phosphorescent paints are used in perfect darkness, their own brightness being very low. Under these conditions the light is no longer perceived by means of the cones of the retina (photopic vision), but by means of the rods (scotopic vision), which are not able to distinguish colors and which have a maximum of sensitivity for radiation of wave-



a b

Fig. 52.—a: Door in daylight. b: In blackout phosphorescent illumination. (*Paint Progress*, **2**, 10, 1940, courtesy of New Jersey Zinc Co.)

length 5150 Å (Fig. 53). Therefore light of a bluish green hue has a greater efficiency in this case than the yellow-green color which is most efficient under normal illumination. This advantage, is frequently counterbalanced, however, by the fact that scotopic vision is almost exclusively restricted to the peripheric parts of the retina, where the images are badly defined. Therefore letters or other signs would have to be larger in order to be legible.[15] On the other hand the human eye is to a very large degree

[15] W. A. Cyr, *Trans. Illum. Eng. Soc.*, **36**, 617 (1941).

capable of dark adaptation which reaches its full value only an hour after the eye has been exposed to bright light. It therefore results that, for a man coming from a brightly illuminated room into the dark, a phosphorescent paint the intensity of which decays constantly appears to grow

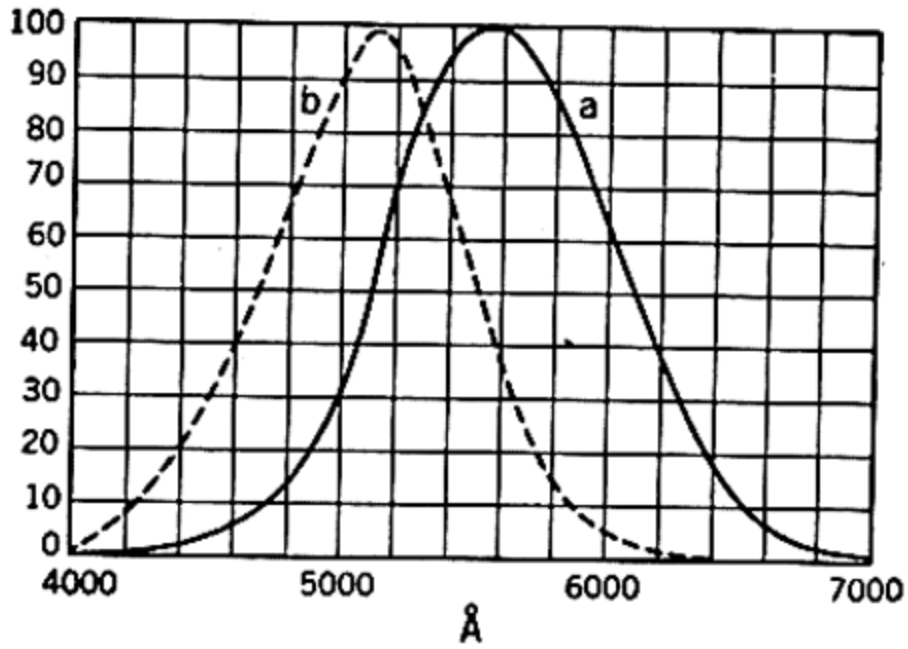


Fig. 53.—Spectral sensitivity of human eye. a: Cone vision. b: Rod vision.

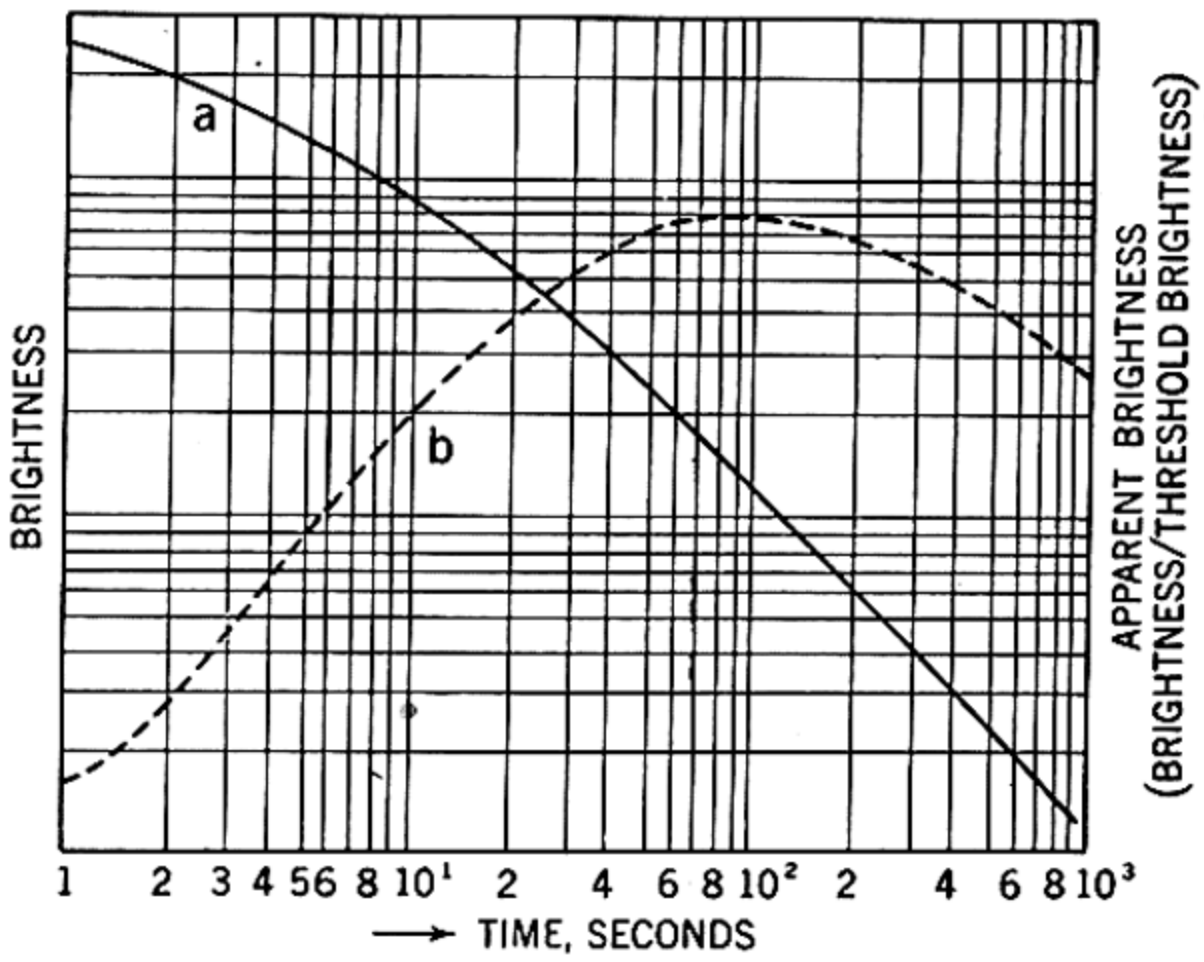


Fig. 54.—Brightness decay and apparent brightness decay of a luminescent paint as a function of time and dark adaptation of the eye (Schilling).

———— Brightness in arbitrary units.

– – – – – Apparent brightness (brightness/threshold brightness).

brighter during the first minutes, and afterwards for quite a time seems to decay less strongly than is objectively true (Fig. 54).[17]

Employment of phosphorescent paints on a very large scale is not to

[17] M. Schilling, *Z. tech. Physik*, **21**, 232 (1940).

be expected for the present because of the rather high price of the material. CaS phosphors cost about $5 per pound and ZnS phosphors from $17 to $48. Accordingly the prices for the finished paints vary between $50 and $200 per gallon, a square foot of painted surface ranging from 20 to 80 cents.

c. Radioactive Self-Luminescent Paints

The ideal luminescent paint would be a source of continuous light emission without an external source of energy.

Ordinary phosphorescent paints prepared with the sulfides of Ca, Sr or Zn have at most an afterglow of not more than four hours. After this period their luminescence has decayed to such low intensities that the phosphor must be re-exposed to an external source of exciting radiation.

As mentioned in Chapter III, α-rays have a very high efficiency for supplying energy to zinc sulfide phosphors. If a radioactive substance emitting α-rays is incorporated in a ZnS phosphor, the luminescence of the phosphor is continuously excited as long as the activity of the radioactive product lasts. Radium has a half-life of over 1000 years. Because of its high price, however, it has in general been supplanted by mesothorium with a half-life period of only 7.9 years.[18] Mesothorium itself emits β-rays, but its disintegration product radiothorium is an α-ray emitter, with a half-life of about two years. Due to its low radiothorium content, the α-ray activity of freshly prepared mesothorium is very small. It increases slowly during the first 4.6 years, when the state of equilibrium between mesothorium and radiothorium is reached. From then on the α-ray activity decreases again, but after 10 years it has not yet fallen below its maximum value by more than about 25%.[19]

Thus the luminosity of ZnS paint activated with mesothorium, after increasing at first, would remain very nearly constant over a relatively long period.

As a matter of fact the mean lifetime of the radioactive substance is of little importance, so long as it is greater than a few years, because of the deterioration of the phosphor itself; its luminescent yield decays at a much higher rate in consequence of the α-ray bombardment. Figure 55 shows a typical decay curve of a radioactive luminescent paint throughout its life.* The initial brightness is proportional to the radium content, which is in general from 0.01 to 0.6 mg. radium bromide (or to its radioactive

* The rising part of the curve which is observed frequently during the first days is probably due to a partial recovery of the loss of luminosity of the paint in the wet state (see below).

[18] L. Meitner, *Physik. Z.*, **19**, 257 (1918).

[19] P. M. Wolf and N. Riehl, *Z. tech. Physik*, **12**, 203 (1931).

equivalent of mesothorium) per gram of ZnS.[20] The rate of deterioration of the phosphor, however, also increases with increasing radium content,[21] so that the luminosity curves for different radium contents cross each other after a certain period of time. After the first six months the luminosity is the same to within 20% for all radium contents, between 0.8 and 0.2 mg. radium bromide per g. ZnS (Fig. 55). In the case of the standard 0.4 mg. composition the luminosity falls within the first year of its life to about one fourth of its initial value; 0.05 mg. of radium produces only a 17% reduction per year; in the case of 0.001 mg. radium per g. ZnS the deterioration does not exceed 1% per year.[22] The deterioration of the radium

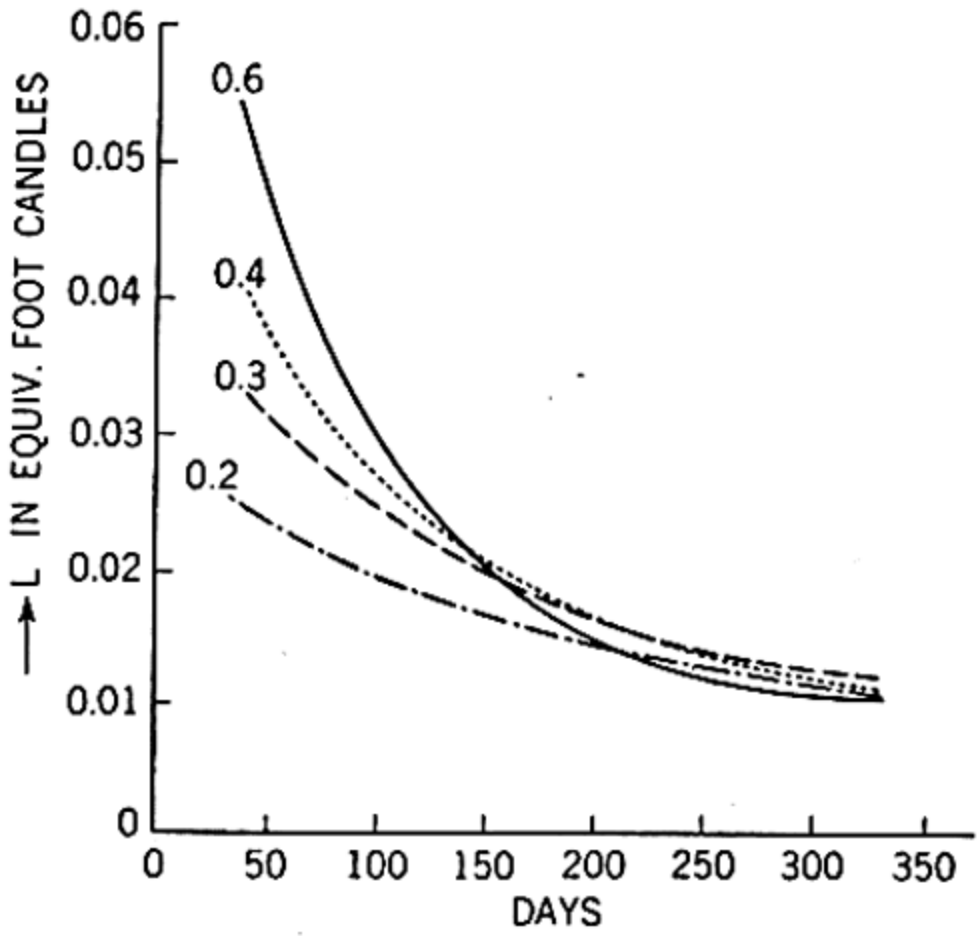


Fig. 55.—Deterioration of luminosity of radioactive paints with 0.6 to 0.2 mg. radium per g. ZnS (Paterson, Walsh, and Higgins).

activated zinc sulfide is due in part to the destruction of the luminescent centers in the crystals, but also to the fact that by this process the compound is blackened and transmits less of the light coming from the deeper layers of the material.

British and German authors report that a quantity of 0.01 mg. radium mixed with 1 g. ZnS is sufficient for a luminous surface of 1.5 square inches with a brightness equal to the brightness produced by a lamp of ten

[20] L. Levy and D. W. West, *Chemistry & Industry*, (J. Soc. Chem. Ind.), **1939**, 457.

[21] E. Rutherford, J. Chadwick, and C. D. Ellis, *Radiations from Radio-active Substances*, Cambridge Univ. Press, London 1930; G. Berndt, *Radioaktive Leuchtfarben*, Vieweg, Braunschweig, 1920; S. C. Lind, *Chemical Effects of Alpha Particles and Electrons*, Reinhold, New York 1928.

[22] C. C. Paterson, J. W. T. Walsh and W. F. Higgins, *Proc. Phys. Soc. London*, **29**, 215 (1917).

candle power at a distance of ten meters or about 32 feet. Thus the specific brightness of the area is 10 microlamberts and the total radiation given off by the whole surface is 0.0001 mean spherical candles.*[22]

For luminous paints manufactured in the United States, the luminous efficiency is rated as 0.5–0.7 watt per candle, corresponding to the α-radiation of 3.6 to 5 g. radium per candle power or to about 0.4 mg. radium bromide for the production of 0.0001 candles.[23]

The actual procedure in the manufacture of radioluminescent paints is usually kept secret by the manufacturers. In principle, however, it is the following: Cu-activated ZnS is mixed in the desired proportion with an aqueous solution of the bromide of radium or of mesothorium. The solution is evaporated and dried at a slowly increasing temperature. Too much heat or fine grinding of the crystals will diminish the luminosity. When dry, the luminous powder is mixed with an adhesive or varnish and applied to whatever surface one intends to render visible in the dark. Very thin layers of paint do not give the full effect. Thicknesses of about one-fiftieth of an inch have to be used. Some commercial preparations cover three square inches of surface per gram of radioactive luminous compound.[24]

The rate of decay of luminosity of a painted surface is noticeably lower than that of the dry powdered compound before application. The initial brightness of the painted surface is also only about one-third to one-fourth the brightness of the compound before application.† A dial painted with a compound containing 0.6 mg. radium per g. will follow approximately the same decay curve and have the same initial luminosity as a powder containing 0.2 mg. radium per g. Hence the maximum radium content for a painted surface is 0.6 mg. per g. ZnS, if the paint is to last for more than 6 months.

If the radium content exceeds 0.1 mg. per g. ZnS, the time interval other surface should be as short as possible. In the wet condition the mixed paint deteriorates very rapidly. The deterioration due to one month's

* Ten microlamberts correspond to about one-hundredth of the brightness of a newspaper satisfactorily illuminated for comfortable reading by artificial light. White paper illuminated by the light of the full moon is of the same order of brightness. This rather low brightness makes exact measurements of the luminosity of radioactive paints somewhat difficult. By using the Wratten filter "Minus Red" in conjunction with a tungsten filament lamp operated at 1.5 watts per candle an approximate color match is obtained for the photometry of radioactive paints. The greenish hue of their light is produced by an emission band between 4250 and 5920 Å with a fairly sharp edge towards the red end.

† This decrease results from a partial absorption of the α-particles in the varnish.

[23] C. H. Viol and G. D. Kammer, *Trans. Am. Electrochem. Soc.*, **32**, 133 (1917); E. Perry, *Paint Varnish Production Mgr.*, **7**, 20 (1932).

[24] W. S. Andrews, *Gen. Elec. Rev.*, **19**, 809 (1916); A. T. Parsons, *Oil Colour Chem. Assoc.*, **12**, 3 (1929); W. Merz, *Protar*, **5**, 17 and **6**, 156 (1939).

delay in painting will be as bad as the loss in luminosity resulting from a three-months' storage of the completed dial.[25]

The most frequent use of radioactive luminescent paints is their application to instrument dials and watches in order to render the figures and graduations visible at night without external illumination. The legibility of the figures depends not only on the quality of the paint but also on the method of its application to the dial. The proportion of width of line to height of letters for maximum legibility should be about one to eight and should, at any rate for letters and figures in which the height is more than five mm., not exceed one to seven. Below this limit experience suggests that the width of line may usefully be increased to one-sixth of the height of the figures.

Besides the use of radioactive paints on dials and handles of watches, they find frequent application for pointers of scientific and technical instruments, revolver and gun sights, fish baits, theater numbers, etc. To a still higher degree than in the case of phosphorescent paints, a large industrial use of the material is restricted by the high price and by the limited supply of radioactive products now at hand. The price of the luminescent radioactive compound ranges from 90 cents to $10 per gram, depending on the content of radioactive salt.

2. Fluorescent Screens

a. Fluoroscopy

Radiation which does not directly affect the eyesight can produce visible images without the intervention of photography by means of a fluorescent screen. Such screens have wide fields of application in x-ray, cathode ray and U.V. light technique.

Because of their greater stability, inorganic materials are used exclusively. If the screens are to be viewed from one side and to be excited from the other side, the support for the luminescent material must, like glass, quartz or mica, be transparent to visible light. Otherwise it may be metal or cardboard.

Two methods are in general use for the preparation of fluorescent screens. In the first, the finely powdered material is suspended in an indifferent liquid,* the mixture is poured evenly upon the supporting plate and when the suspension has settled, the plate is tilted cautiously so that the liquid is decanted, leaving the sediment on the plate. In the second, the material is dusted through a sieve or muslin gauze upon the plate which has been coated with some kind of binder like sodium silicate. If

* Water is frequently employed but its use is not very advantageous, since the last remnants are difficult to evaporate. Benzene, or alcohol, is better in this respect.

[25] J. W. T. Walsh, *Proc. Phys. Soc. London*, **39**, 318 (1926).

the screen need not stand heating and is not to be used inside of a vacuum tube, the wetted gelatin side of a clear photographic plate or film is a very useful support for this second method of preparation.*

The resolving power of a fluorescent screen made of finely ground zinc sulphide powder is, under a microscope, of the order of 30 μ. It can be increased to about 10 μ if the screen is made of a well-polished mosaic of small zinc sulphide single crystals which can be produced with good luminescence properties, with surfaces of about one square millimeter.[26]

If a curve or another image produced on a fluorescent screen, of an oscillograph for instance, has to be recorded on a photographic plate, it is better to take a contact photogram than to project the fluorescent image through a lens system upon the plate. The necessary time of exposure is shorter and thus the time resolving power, in the case of a moving image, is a good deal greater when the contact method is used.[27]

The strong green fluorescence of a barium platinocyanide screen under x-ray excitation led to Roentgen's great discovery, and barium platinocyanide screens remained in general use for the observation of x-rays over a long period. They are almost completely discarded at present, mainly because of their high cost. The well-known sulfide phosphors seemed to be unsuitable for the purpose because of their strong and long lasting afterglow which prevents the observation of the images of moving objects. The x-ray luminescence of pure $CaWO_4$ is quite free from afterglow and therefore it prevailed for a time in the manufacture of x-ray screens, but its energy yield is not very high and its luminous efficiency is still lower because of the blue color of the fluorescence. The use of $CdWO_4$, which has a more whitish blue emission, is somewhat more advantageous in this respect.[28]

However, since Levy and West[29] showed that the afterglow of ZnS phosphors is almost completely quenched with negligible loss of fluorescence by addition of a minute quantity of nickel, silver activated ZnCdS phosphors have practically superseded all other material in the manufacture of x-ray fluoroscopic screens. Their yellow-green fluorescence corresponds to the optimum visual sensitivity and thus the screens are nearly ten times as bright for subjective observation as the older $CaWO_4$ screens. Because of the logarithmic response of the human eye, weak intensities show up much more distinctly on such a screen than on a photographic image.

* For the production of a "thermoluminescent screen" see footnote on page 156.

[26] M. v. Ardenne, *Z. tech. Physik*, **20**, 239 (1939).
[27] M. Knoll, *ibid.*, **12**, 54 (1931).
[28] B. Cassen, *J. Applied Phys.*, **12**, 410 (1941); L. Levy and D. W. West, *Trans. Faraday Soc.*, **35**, 128 (1939).
[29] L. Levy and D. W. West, *J. Elec. Eng.*, **79**, 11 and 25 (1936).

The front side of the screen is protected by a varnish transparent to x-rays and the fluorescent powder is backed with heavy lead glass which transmits the fluorescent light, but shields the observer from the dangerous action of the x-rays not absorbed in the screen material.

Of the many important applications of fluorescent screens in cathode ray tubes, the most interesting ones are probably the following three: oscillographs (including electrocardiographs), television receivers and electron microscopes. All these devices are cathode ray tubes with, in general, an indirectly heated cathode at one end* and a fluorescent screen at the other end of the highly evacuated tube. The electron beam emitted by the cathode is focused upon the screen by means of so-called electrostatic or magnetic lenses exactly as a light beam is focused by glass lenses.†

In oscillographs and television tubes the lenses are so constructed that a reduced image of the cathode is formed, appearing as a small luminous spot on the screen. Before reaching the screen, the cathode ray beam is deflected from its straight path by rapidly changing electrostatic or magnetic fields, so that the luminescent spot changes its position on the screen continuously.

In oscillographs the intensity of the cathode rays, as defined by current density and voltage, and thus the brightness of the luminescent spot are constant. Two electric or magnetic fields, deflecting the cathode rays in directions perpendicular to each other, are produced by the alternating voltage and current under investigation, and, following these varying forces, the spot describes a curve on the screen. If the same curve is repeated periodically many times with great speed, the eye perceives a curve at rest. Under these conditions a certain persistence of the luminescence increases the steadiness of the image and is advantageous. If, on the other hand, the shape of the figure is rapidly changing, the period of the afterglow must be shorter than the period of the alternating fields. Thus for different purposes oscillographs are equipped with screens of different quality. Long or medium persistent afterglow is provided by green phosphorescent ZnS or mixed ZnS-Zn_2SiO_4 phosphors with white luminescence. If no afterglow is desired, blue fluorescing $CaWO_4$ is employed, especially

* Electron microscopes are frequently equipped with a cold cathode and a gas filled discharge chamber separated from the highly evacuated observation tube by a wall with a narrow pin hole for the transmission of the electron beam (see Fig. 60).

† Electrostatic lenses are coaxial cylindrical electrodes charged to positive or negative potentials; magnetic lenses are coils carrying a constant electric current. Both devices are able to deflect cathode rays For details concerning "electron optics" special books should be consulted, *e.g.*, L. M. Myers, *Electron Optics*, Van Nostrand, New York 1939. A resumé may be found in *J. Applied Phys.*, **10**, 765 (1939).

if the image is not only to be viewed subjectively but is to be reproduced on a photographic plate.*[30]

In television receiving tubes the movement of the spot in horizontal and vertical directions is caused by auxiliary alternating currents or voltages, so that the whole screen is scanned, line by line, within $_3{}^1{}_0$ of a second. In the tubes manufactured in the United States the screens usually have

Fig. 56.—Television receiving tube. (Courtesy of R. C. A. Co., Camden, N. J.)

diameters of 7, 9, or 10 inches. The surface of the image, which is covered by the moving spot, is rectangular, the ratio between height and length being equal to ¾ (Figs. 56, 57). This rectangle is scanned by the electron

* The choice of the screen material also depends to a certain degree on the accelerating voltage applied to the tube (see pages 29 and 48).

[30] E. W. Engstrom, *J. Applied Phys.*, **10**, 461 (1939).

beam in 441 lines, and each line in 588 steps, so that each individual irradiation lasts only $\frac{1}{30} \cdot 441 \cdot 558 =$ approximately $\frac{1}{7,000,000}$ of a second. The intensity of the electron beam and hence the luminosity of the spot is modulated by the varying energy of the incoming wave. If the transmitted image is moving, the persistence of the luminescence must be shorter than the period after which the spot returns to its initial position, that is, it must not exceed $\frac{1}{30}$ of a second. Photographic reproduction is

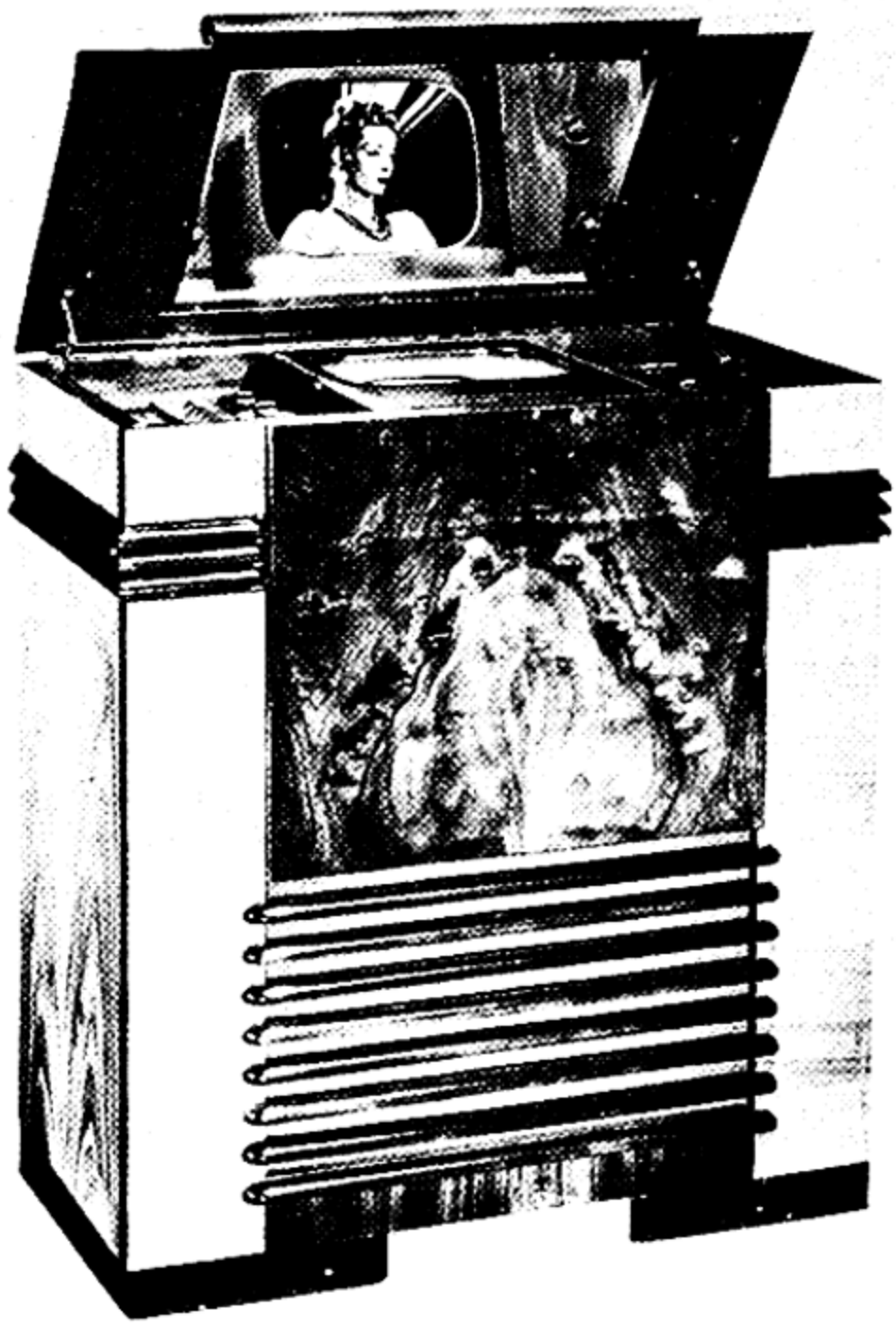


Fig. 57.—Television receiver mounted. (Courtesy of R. C. A. Co., Camden, N. J.)

not to be taken into account, but high intensity for visual observation is wanted. Green fluorescing ZnS(Cu) phosphor, with a "Ni-killer," would be the most brilliant material, but there is a strong tendency to produce the images in black and white by the use of less bright mixed phosphors. This was rather a concession to a prejudice, as long as it was only a question of "black and white." In a room of very low overall illumination with only one relatively bright screen, the eye loses the sensation of color very soon and perceives only the contrast between light and dark as equivalent

to white and black. The problem is a very different one if television in natural colors is to be achieved. In the most promising apparatus so far designed for this purpose, the image of the original object is projected through a colored filter upon the photosensitive surface of the television camera. From there it is transmitted to the receiver tube as usual. However, the color filter in front of the camera is replaced by one of another color as soon as the whole photosensitive surface of the camera has been scanned, so that alternately images corresponding to three different colors are transmitted in rapid succession. The images formed by the cathode rays on the fluorescent screen of the receiver are viewed through color

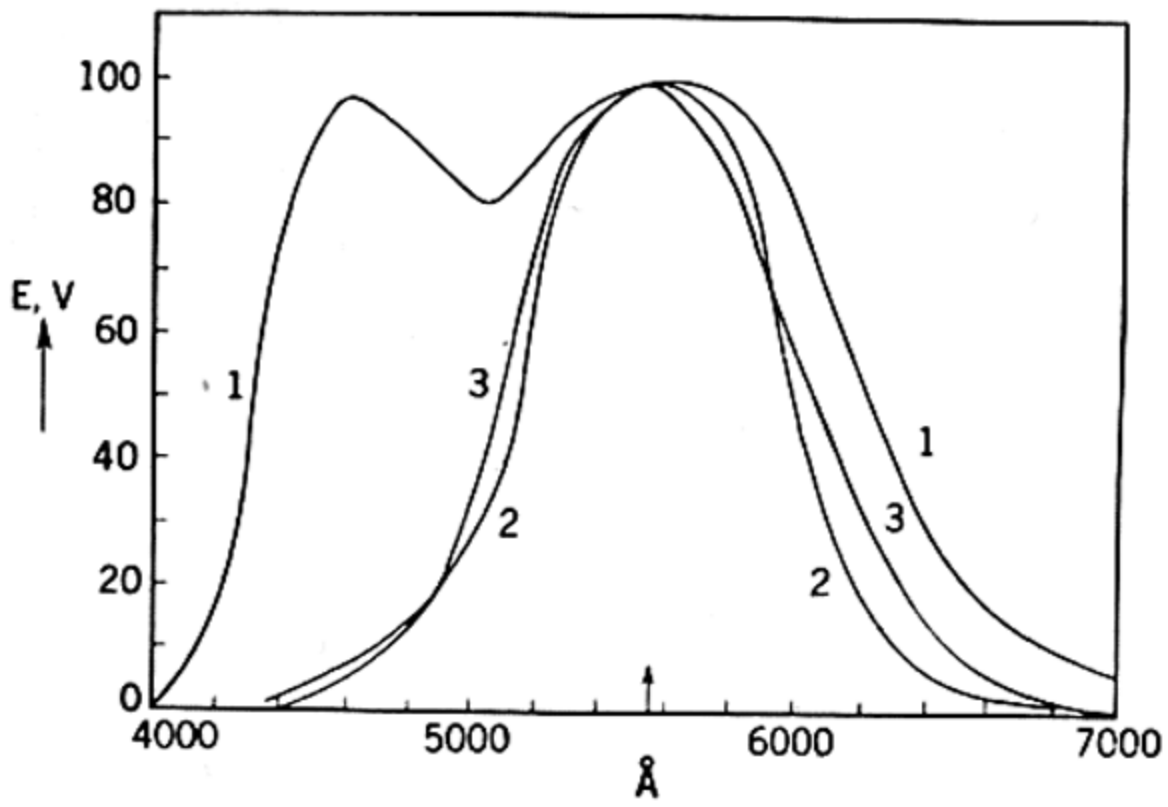


Fig. 58.—White fluorescent screen for television (three component sulphide phosphor) (Leverenz). 1: Energy distribution of the fluorescence spectrum. 2: Visibility of the same spectrum. 3: Visibility curve of daylight.

filters which are exchanged synchronously with those in front of the camera. In both cases the color filters, a red, a green and a blue one, have the shape of sectors and are mounted on a rotating disk. If images in natural colors are to be produced by this device, the fluorescent screen must not only respond to the cathode ray excitation with "white light" but the spectral distribution of the visibility of this white light must be similar to that of daylight. This is very nearly attained by a mixture of three ZnCdS phosphors, as shown in the curves of Figure 58.[31] In the red part of the spectrum the curve for the fluorescent light is still below the daylight curve. Thus all red objects will appear either too dark (in the case of pure spectral reds) or too yellowish on the screen.

[31] H. W. Leverenz, *J. Optical Soc. Am.*, **30**, 309 (1940).

In electron microscopes,[32] the electric and magnetic lenses are designed so that a greatly enlarged image, either of the cathode itself or of some object diffracting the cathode rays, is formed on the screen (Figs. 60 and 61). In the first case the cathode acts as a "self-luminous" object. The various parts of the cathode surface produce more or less luminous parts

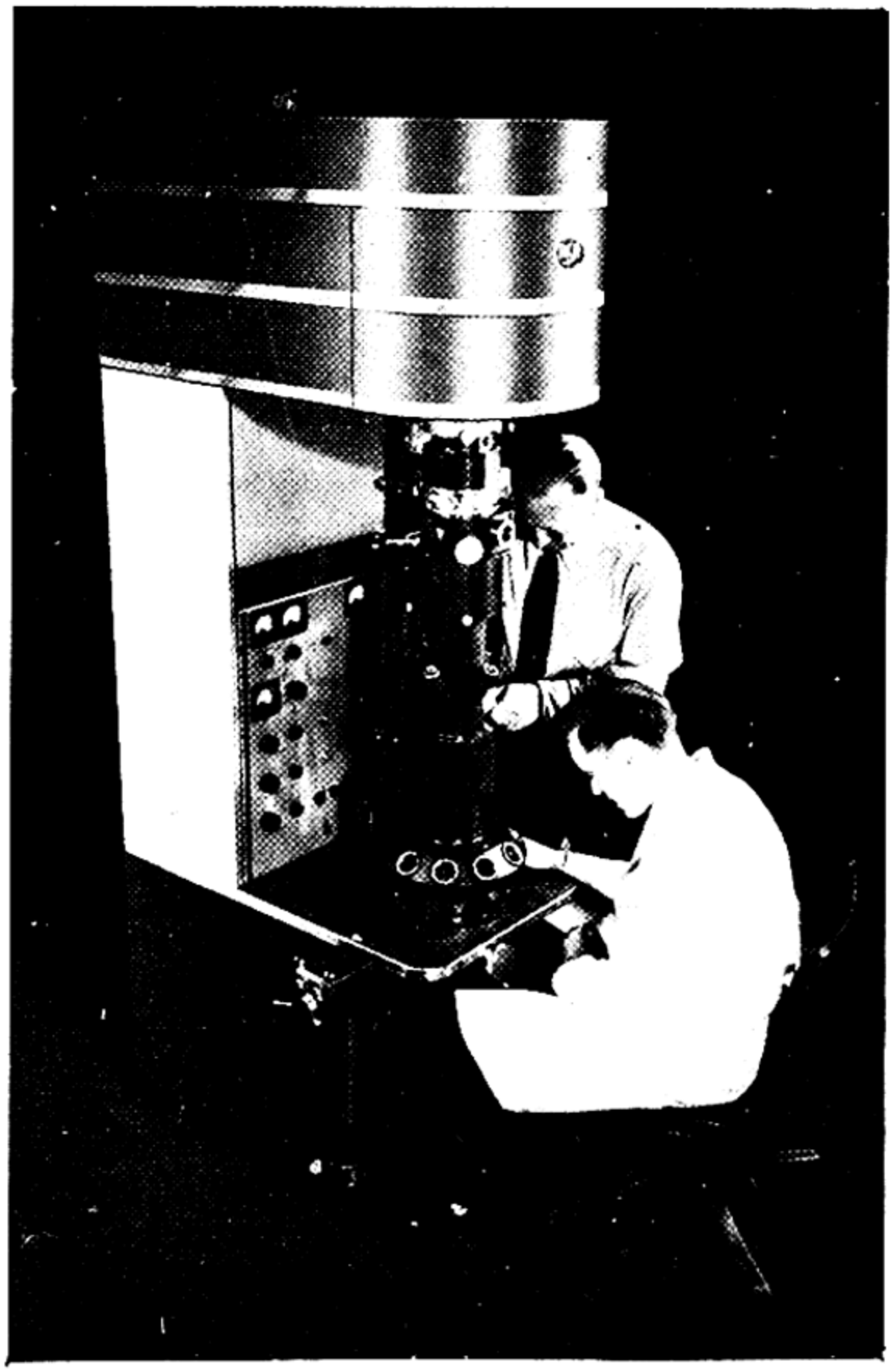


Fig. 59.—Electron microscope. (Courtesy of R.C.A. Comp., Camden, N. J.)

of the image on the screen, according to their electron emissivity. Since the object is at rest, the question of afterglow is not important, nor is the esthetic question of the fluorescence color. ZnS(Cu) phosphors are the

[32] E. Ruska and M. Knoll, *Ann. Physik*, **12**, 607 (1931); T. Brueche, *Naturwissenschaften*, **20**, 49 (1932); V. K. Zworykin, J. Hiller, and A. W. Vance, *Elec. Eng.*, **19**, 167 (1941); V. K. Zworykin, in *Science in Progress*, Chapter IV, Yale Univ. Press 1941.

most favorable for visual observation and ZnS(Ag) or $CaWO_4$ for photographic reproduction of the image. In the latest electron microscopes, however, photograms are no longer obtained by recording the image formed on a fluorescent screen by means of a photographic camera, but a photographic plate is placed immediately below the fluorescent screen within the microscope itself and the screen can be pivoted so that it either receives the electron image or uncovers the plate for an exposure. While the maximum resolving power of a microscope using visible light, for instance a fluorescence microscope, allows distances not below 1200 Å to be distinguished, objects as small as 20 Å can be resolved by a modern electron microscope.

Of other applications of fluorescent screens in cathode ray tubes the so-called image converter or intensifier seems to promise much for the future, though it has not yet been used to a great extent.[33] It is related to the electron microscope in the same way as a telescope is to an ordinary microscope, the lenses producing a somewhat reduced image of the cathode on the fluorescent screen. In these tubes the cathode is a photosensitive surface upon which a real image of some object is formed by means of light rays. Either the cathode is transparent and the light impinges on its reverse side, or the image is projected obliquely upon the cathode from the front side (Figs. 62 and 63). The electron emission is proportional to the light intensity at every point of the photocathode, and thus an image of corresponding intensity distribution is reproduced by the electron lenses on the fluorescent screen (Fig. 64). Materials are available which respond to photoelectric excitation by infrared light of 1.2 μ. Hence it is possible

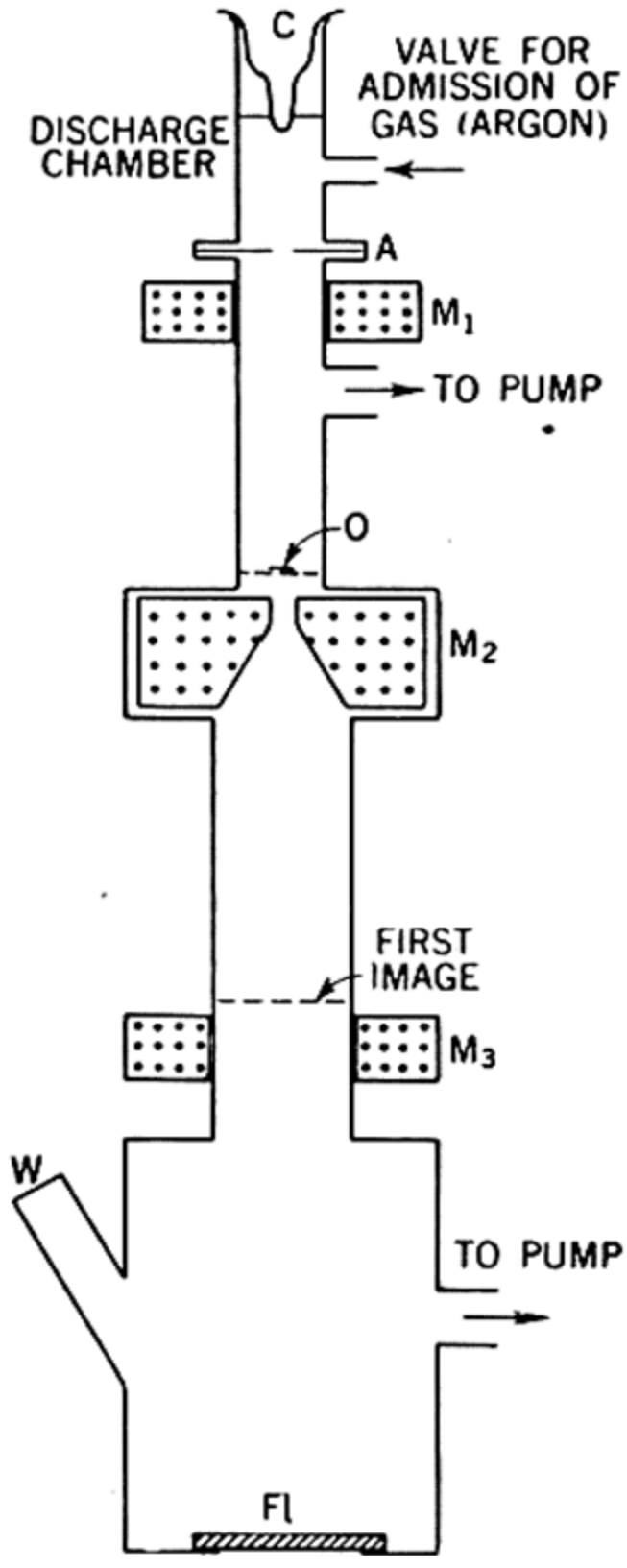


Fig. 60.—Schematic representation of electron microscope.

C: Cathode.
A: Anode with small hole.
O: Object to be investigated.
M: Magnetic lenses (M_1 condenser; M_2 and M_3 "objectives").
W: Observation window.
Fl: Fluorescent area.

[33] W. Schaffernicht, *Z. tech. Physik.*, **17**, 597 (1936); V. K. Zworykin, *J. Inst. Elec. Engrs. London*, **79**, 1 (1936).

to convert infrared images into visible images.* As a matter of fact the first idea of these converters was conceived with the purpose of providing better sight for aviation in hazy weather by means of infrared rays.

Fig. 61.—Image produced by electron microscope of *Mycobacterium tuberculosis.* (Courtesy of R. C. A. Co., Camden, N. J.)

The excellent results obtained by photography under such conditions are well known.

* The idea that in the future it might become possible with more suitable photosensitive materials to receive images produced by irradiation with long-wave infrared radiation is a fallacy, nevertheless. A material responding to "heat radiation" would be characterized by a work function so small that at room temperature its thermal electron emission would be very strong and thereby the images would be completely fogged. At room temperature, 9 per cent of all molecules have a kinetic energy greater than the energy of the photon of 10 μ or 0.12 e.v.

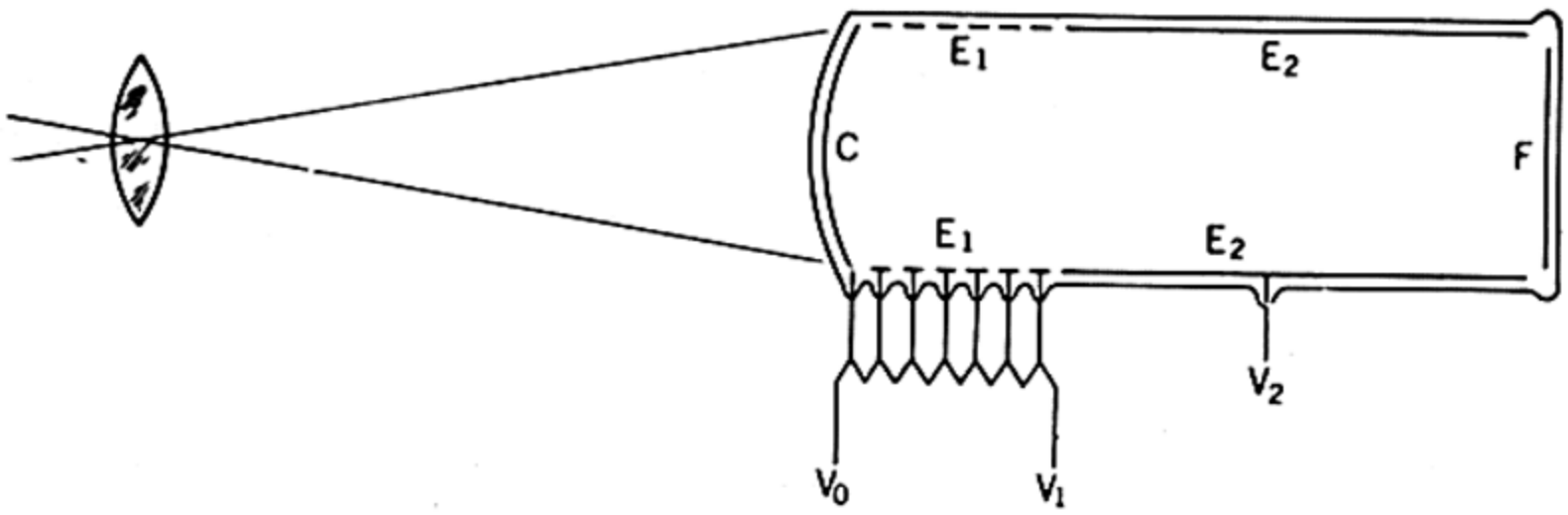


Fig. 62.—Image converter illuminated from behind (Zworykin).

E_1: Electrostatic ring lens. E_2: Electrostatic lens.
C : Photocathode. F : Fluorescent screen.

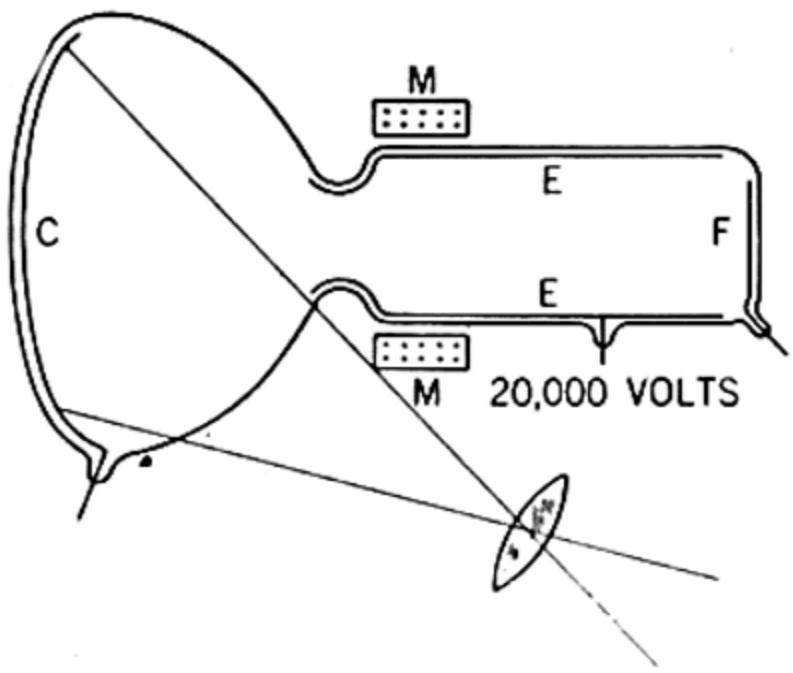


Fig. 63.—Image converter illuminated from front (Schaffernicht).

E : Electric lens. C: Photocathode.
M: Magnetic lens. F : Fluorescent screen.

Fig. 64.—Comparison of images from tubes with flat (left side) and curved (right side) cathodes. (Courtesy of R. C. A. Co., Camden, N. J.)

In principle it is possible to amplify the intensity of the first image as much as one desires by applying high voltage acceleration to the converter and using several converters in series. But for various reasons no very large amplification can be attained in this way.*

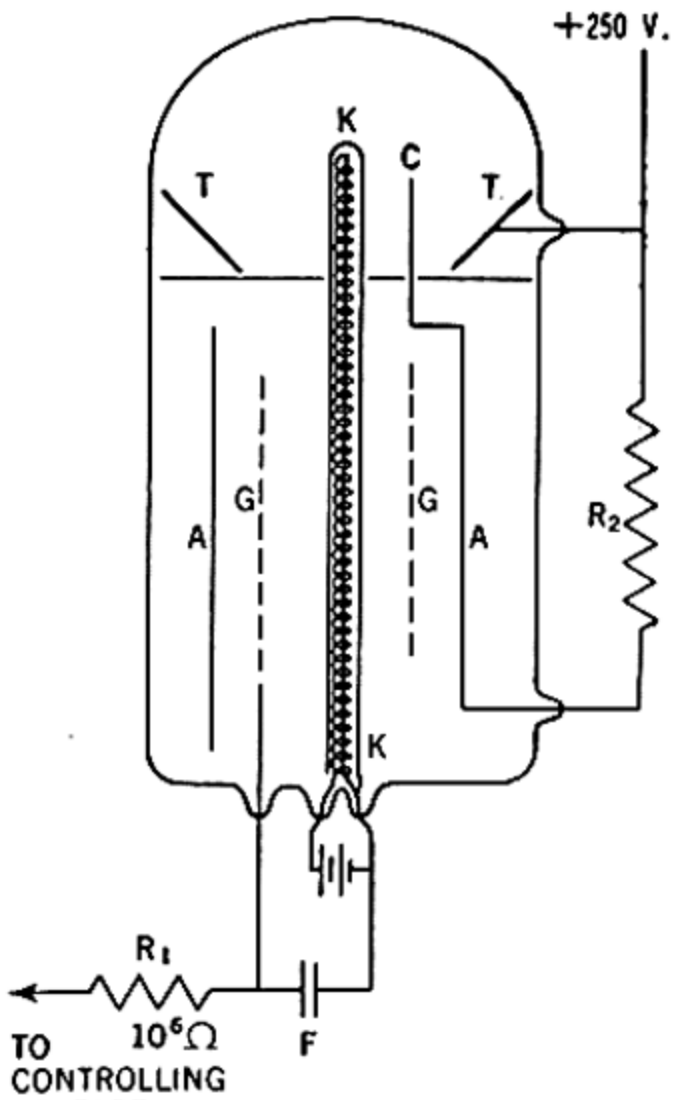


Fig. 65.—Electric eye.

T: Fluorescent target.
A: Anode.
F: Capacitance of 0.1 μf.
G: Grid.
C: Controlling wire.
K: Indirectly heated cathode.
R_1, R_2: Resistors.

The "electric eye" or indicator tube has probably already found larger fields of application than any other apparatus with a fluorescent screen excited by cathode rays. Many radio receivers are equipped with electric eyes for the purpose of exact tuning. In these tubes the fluorescent target has the shape of a conical ring and serves as anode. The indirectly heated cylindrical cathode (*K* in Fig. 65) is coaxial with the anode. Between anode and cathode and parallel to the latter a thin wire *C* acts as "ray control electrode." *C* is connected to the plate of an amplifier tube. With no plate current in the amplifier, *C* is at the same potential as the fluorescent target *T* and does not influence the electron current from the cathode to the screen. With increasing plate current, or with decreasing negative potential of the amplifier grid *G*, *C* is charged negatively with regard to *T*. The electrons in the "electric eye" are deviated from their radial path and the wire *C* casts a shadow upon the screen. This shadow becomes the broader, the higher the negative potential of *C* or the lower the negative potential applied to the grid *G*. The shadow angle, varying between 0° and 90° is a measure of the grid

* The amplification is limited by at least two reasons. The photoelectric yield is at its best of the order of one electron per 100 impinging photons, and the fluorescent yield for cathode ray excitation does not exceed 10 per cent. Taking the energy of the primary photons as 2.5 e.v., corresponding to a wave-length of about 5000 Å, an accelerating potential of 10,000 volts would produce, under these rather optimistic assumptions, not more than a fourfold amplification if the response of the phosphor remains proportional to the electron energy up to 10,000 volts. Further, a very bright image produced on the fluorescent screen would illuminate the photocathode at the opposite end of the tube and generate an additional electron emission which would again fog the image.

potential. If a high frequency alternating potential is to be measured, the shadow angle opens and closes with the same frequency, but the observer perceives a sector of permanently reduced intensity with an angle corresponding to the maximum voltage of the alternating voltage. In the industrial construction of electric eyes, the fluorescent target and the amplifier are contained in one tube with the same central cathode providing the electron currents for both. Apart from radio receivers electric eyes serve as null indicators for alternating currents in Wheatstone bridges and similar devices.

Photoluminescent screens for the production of visible images by the conversion of ultraviolet or infrared radiation are of relatively smaller importance. Quartz spectrographs are usually equipped with a matt glass which consists at least in part of canary glass in order to facilitate the focusing of the ultraviolet region of the spectrum. The response of canary glass to short wave ultraviolet light below 3000 Å is, however, rather poor.* A glass plate coated on the front side with a thin transparent layer of fluor-ammonium uranyl fluoride gives much more satisfactory results. This compound is very useful in every case where a beam of short wave U.V. light has to be focused upon a given spot.

The fluorescence of a screen excited by the radiation from a Sc 2537 mercury arc lamp† makes it possible to discover the presence of mercury vapor in the atmosphere of factories, mercury mines, etc. The lamp radiation is strongly absorbed by mercury vapor and the fluorescence intensity is reduced accordingly. The fluorescent material used for this purpose should, like zinc silicate phosphors or calcium tungstate, respond to exciting light of wave-lengths below 3000 Å only. In combination with a fluorophotometer the method can be used for a quantitative determination of the mercury vapor concentration in the air; it is more sensitive and simpler than any other test.

In a more qualitative way the presence of mercury in a liquid‡ or a solid can be ascertained by evaporating the liquid or heating the solid, so that the vapor ascending in front of the lamp casts a cloud-like shadow on the fluorescing screen.

Organic vapors contaminating the air in some chemical factories, benzene for instance, have the property of absorbing the Hg line 2537 Å, and thus

* This is evidently caused by the fact that too great a part of the impinging light is absorbed by other components of the glass which yield a much less intense fluorescence than do the uranyl ions. The change in fluorescence color of canary glass from yellow green to blue green is easily observed when the wave-length of the exciting light is 3650 or 2537 Å respectively.

† See page 38.

‡ For instance in a secretion from the human body.

their presence can be traced at concentrations at which they would not be recognized by other means. In this case a hot mercury lamp which emits the line 2537 Å as "self-reversed" can be used as light source. In mercury vapor of low density the radiation from such a lamp would be very little absorbed or even not absorbed at all. This provides the means of discriminating between the presence of mercury vapor or some organic vapor in the air.

The transparency of a few centimeters of atmospheric air to light rays of wave-lengths between 1240 and 1100 Å* was demonstrated by Lyman[34] by means of the thermoluminescence of a $CaSO_4$ (Mn) screen.† After irradiation with the light from an iron spark, the screen emits a yellow "thermophosphorescence" when heated in a dark room to about 180° C. The radiation by which the thermophosphorescence can be excited is cut off by a fluorite plate which is transparent for "Schumann ultraviolet" down to 1240 Å. It is transmitted through a LiF plate whose absorption begins at 1100 Å. The method is also serviceable for the selection of the best specimens of LiF, which alone transmits the radiation of the wave-length interval 1200–1100 Å.

The afterglow of certain sulfide phosphors like ZnS(Cu) or CdS(Mn) is strongly quenched by infrared radiation. A screen coated with one of these phosphors remains fairly bright over a considerable period after exposure to blue or violet light. If during this period parts of the screen are irradiated with red or infrared light, these parts lose the stored excitation energy and appear dark on a lighter background. In general this method is not used much except for lecture room demonstrations. It has been recently patented, however, for the demonstration of a positive image of a photographic negative. The negative is projected upon the phosphorescent screen through a dark red filter. The parts of the negative which are less dense on the plate transmit more red light and the corresponding parts on the screen are more strongly quenched. The densest part of the negative gives the most complete protection against quenching.

The different methods using fluorescence for the production of visible images by means of invisible radiations can be classified in the following way:

1. The object is made fluorescent itself by ultraviolet light or cathode

* Atmospheric air is perfectly opaque to light of wave-lengths between 1840 and 1250 Å.

† A paste of finely powdered $CaSO_4$ with addition of 1 to 5 per cent of $MnSO_4$ and water is smeared on a copper strip and heated for several minutes to red heat. The screen is made thermoluminescent by exposure to light of all wave-lengths between 1300 and 140 Å, as was shown by the use of a vacuum spectrograph.

[34] Th. Lyman, *Phys. Rev.*, **48**, 149 (1935).

rays and can be directly visualized, as for instance in the fluorescent microscope.

2. The object remains invisible but emits or scatters an invisible radiation which produces a visible image on a fluorescent screen.

3. The object emits invisible infrared radiation which quenches the phosphorescence of an excited phosphorescent screen and so forms a negative image on the screen.

4. The object is more or less opaque to the incident rays (x-rays in this instance) and throws a shadow image on a screen, which would be excited uniformly to fluorescence without the intervening object.

5. The stimulation of luminosity of an excited "frozen-in" phosphorescence by long wave-length radiation might also be used, but it does not seem to have found any practical application so far.

b. Application of Fluorescent Screens to Photography

When the photographic silver bromide emulsion responds poorly or not at all to the impact of a radiation, this failure can frequently be remedied by the use of "intensifying" fluorescent coatings. The fluorescent substance is excited by the primary radiation. It is on the other hand in direct contact with the photographic plate or film. Thus a contact image of the luminescent screen is superimposed upon the image which would have been produced on the plate by the action of the primary radiation itself. A certain loss in sharpness is unavoidable in images obtained by this method, but it is negligible in general. The boundary lines of a figure are broadened to not more than a few hundredths of a millimeter. It is of course essential that the wave-length of the fluorescent light corresponds to the highest spectral sensitivity of the photographic emulsion (between 4500 and 3000 Å).

The method is used for x-rays which are too slightly absorbed by the emulsion, and for ultraviolet light of wave-lengths below 2300 Å which is too greatly absorbed by the gelatin.

$CaWO_4$ screens were once exclusively employed for x-ray intensification screens and are still widely used. Recently ZnS(Ag) with a "Ni-killer" was proposed instead. It emits a brilliant blue fluorescence and for soft Roentgen rays, at 40 kv., it is about six times as effective as $CaWO_4$. However, when the voltage of the x-ray tube is raised to 80 kv. or more, the ZnS(Ag) screens are only slightly more efficient than the tungstate screens, and their resolving power decreases a good deal, while it remains unchanged for $CaWO_4$.[35] With a doubly coated film and a $CaWO_4$ screen

[35] P. Wiest, *Z. tech. Physik*, **16**, 53 (1935).

on either side the time of exposure is reduced to about one-tenth of the time required without the screens.

The use of so-called Schumann plates with an emulsion very poor in gelatin is not always convenient for ultraviolet spectrography. Therefore Duclaux and Jeantet[36] proceeded to "sensitize" ordinary photographic plates by coating them with a fluorescent lubricating oil. Since this first suggestion, all kinds of fluorescent liquids, mineral and vegetable oils, vaseline, and aromatic hydrocarbons have been recommended for this purpose. It is important that the fluorescent agent covers the surface of the plate homogeneously. Therefore it is dissolved in an easily evaporated solvent like alcohol or benzene. If solutions of solid hydrocarbons are used, they must be prevented from crystallizing after evaporation of the solvent, because this would occur in irregularly distributed patches.* After exposure and before development of the plates the sensitizing oil or hydrocarbon must be removed by an adequate solvent. Oil sensitized films give good results through the whole Schumann U.V. down to about 1000 Å. Their efficiency decreases in the region between 1000 and 500 Å, but in this region, from 1000 to 200 Å and probably even to much shorter wave-lengths, intensifying screens of the type used with x-rays are quite satisfactory. $CaWO_4$, $MgWO_4$ and Zn_2SiO_4 have proved to be about equally serviceable. The screens can be prepared by depositing a thin layer of the finely powdered material from a suspension in water on the gelatin side of a clear photographic film. The film is mounted afterwards in the plate-holder in front of the plate.[37]

While the sharpness of the images is not quite as good on plates sensitized with fluorescent material as on Schumann plates, they are much superior as far as the correct reproduction of relative intensities of spectrum lines is concerned. For the reasons enumerated on page 56, the density of the photographic negative produced by a fluorescent sensitizer is proportional in every part of the spectrum to the number of quanta contained in the impinging radiation. Thus heterochromatic photographic photometry is directly achieved without any supplementary measurements.

* A series of fluorescent sensitizers have been investigated by Allen and Franklin. The following modification of one of their formulae has been found very serviceable. 1 g. of fluorene and 10 drops of paraffin oil are dissolved in a mixture of 25 cc. ethyl acetate and 25 cc. benzene. After evaporation of these solvents the fluorene remains dispersed in the paraffin oil and does not crystallize. Before development the plate must be rinsed, first with benzene and then with alcohol. A fluorescent ultraviolet sensitizer is produced commercially by Eastman Kodak and the same manufacturers have plates sensitized for the U.V. on the market.

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[36] J. Duclaux and P. Jeantet, *J. phys. radium*, **2**, 158 (1922); A. J. Allen and R. G. Franklin, *J. Optical Soc. Am.*, **22**, 467 (1931).

[37] N. C. Beese, *J. Optical Soc. Am.*, **29**, 278 (1939); T. Suga and M. Kamiyana, *ibid.*, **31**, 592 (1941).

The photographic reproduction of fingerprints is facilitated in certain cases by the use of fluorescent materials. Even when dusted over in the usual way with an adhesive powder, fingerprints on a multicolored background show up very poorly on a photograph. If the powder is replaced by finely pulverized anthracene which adheres particularly well to the details of the finger impressions, and if the excess powder is carefully dusted off, the fingerprints are distinctly brought out against a uniformly dark background on a photograph taken with black light.

Two processes called "luminography" by Vanino[38] were intended for the reproduction of prints by means of contact photography. In the first method the print is sandwiched between an excited phosphorescent screen and a photographic paper. In the second method the screen is placed between the photographic paper and the print and the fluorescence is excited by a radiation uniformly illuminating the reverse of the print. The print must transmit in the first case a part of the phosphorescent light and in the second case a part of the exciting radiation, and in both cases negative images are produced.

While this luminography has not found any noteworthy application, a very similar process may become very important for the reproduction of blueprints by contact photography. As a matter of fact the new process is a combination of Vanino's two kinds of luminography. The lines on the original drawing must be so solid that they are completely opaque to the exciting radiation. The drawing is laid upon a phosphorescent screen and the phosphorescence is excited by radiation which has passed through the drawing.* Thus the parts of the screen covered by the black lines of the drawing remain black and appear as white lines on contact photographs taken subsequently from the screen. An advantage of the method is that it may be repeated as often as one wants without wetting the original drawing or the copies, so that no distortion upon drying has to be taken into account.

Another interesting application of fluorescent screens to photomechanical reproduction has been developed lately by B. Berry. The purpose of the method is to eliminate the screen pattern (the halftone dots) from the background or other parts of a picture which are not covered by the drawing itself and are wanted to appear white on the reproduction. These parts are brushed over with a paint which is white in daylight but is excited to a bright blue fluorescence by black light. A negative is taken of the drawing in the usual way through a halftone screen under white light il-

* If the sheet with the original drawing is not transparent to ordinary light, x-rays must be used for excitation. In this case the drawings must be made of thick lead lines.

[38] L. Vanino and A. Menzel, *Chem. Ztg.*, **50**, 225 and 651 (1926).

a

b

Fig. 66.—Reproduction of image. a: With half-tone dots on background. b: With half-tone dots on background removed. (Courtesy of Mr. B. Berry, San Francisco, Calif.)

lumination. Then the halftone screen is replaced by a glass opaque to U.V. while all other parts are left in place and a second exposure made on the same plate with U.V. illumination. Thus the developed negative becomes uniformly black in all parts where the original drawing was

covered with fluorescent paint, and correspondingly these parts are white without any screen pattern on the finished reproduction (Fig. 66).

The reproduction of infrared spectra by contact photography of a "quenched" phosphorescent screen has not much practical value, since photographic plates sensitized up to 12000 Å are on the market.*

If fluorescence has proved itself very helpful to photography in many respects, it can occasionally produce rather unwelcome effects. Some of the light filters which are placed in front of the objective for color photography or for photography of snow landscapes, in order to reduce the blue-violet and near U.V. radiation, are fluorescent under the action of the absorbed light.† Therefore they are apt to fog the plates or films.[39] Other filter glasses fulfilling the same purpose are free from this defect and the filters should be selected accordingly.

3. Fluorescent Lamps

Fluorescent lamps are essentially gas discharge lamps with a thin transparent coating of a luminescent material on the interior of the glass walls. The invisible ultraviolet radiation generated by the discharge is thus converted into visible light.‡

Like all modern low voltage gas discharge lamps, low voltage fluorescent lamps carry, at the two ends of a tubular bulb, electrodes consisting of coiled tungsten wire. These are coated with an alkaline earth oxide emitting electrons at rather low temperatures. The necessary heat is supplied by the discharge itself. In order to start the discharge, the electrodes must be preheated by passing the current directly through the filaments of the two electrodes which are connected in series. The switch making this connection opens automatically when the electrodes are sufficiently hot, and allows the arc to strike (Fig. 67).

* The "quenched phosphor" method is supposed to go somewhat beyond this limit, as far as 14,000 Å (1.4 μ). For the reasons explained on page 152 it is not possible to find a phosphor by which much greater wave-lengths could be rendered visible. A phosphor which would be quenched by the action of 10μ or even 5μ rays would not show any appreciable afterglow. The same principle must be applied to photography itself, as has been pointed out by Czerny.

† Examples are the U.V. absorbing filters stained with aesculin, which are practically colorless, and some of the Jena yellow filter glasses.

‡ While it seems that lamps of this kind alone are used in America, the last fluorescent lamps manufactured by the Dutch firm Philips of Eindhoven were of an essentially different type. They consisted of a small mercury discharge tube about 3.5 cm. long similar to the burner of the H4 Hg lamps. This tube was surrounded by a spherical glass bulb with a diameter of 15 cm. The phosphorescent material was coated on the inside of the glass bulb. No data are available for a comparison between the properties of these lamps and the normal fluorescent lamps.

[39] H. Bäckström and R. Johansson, *Z. wiss. Phot.*, **36**, 194 (1937).

Because of their negative current-voltage characteristic the lamps require a choke coil as current limiting ballast. Owing to the interruption of the electrode heating current the choke generates a short kick of high potential which is sufficient to start the gas discharge.

In general the lamps contain argon at a pressure of about 4 mm. and in addition a small quantity of mercury vapor at a pressure below 0.01 mm. Under these conditions the mercury atoms practically alone are excited to light emission. Current density, and thereby the temperature and the vapor pressure are so regulated that about 50 to 60 per cent of the resulting radiation is concentrated in the mercury resonance line 2537 Å.*[40]

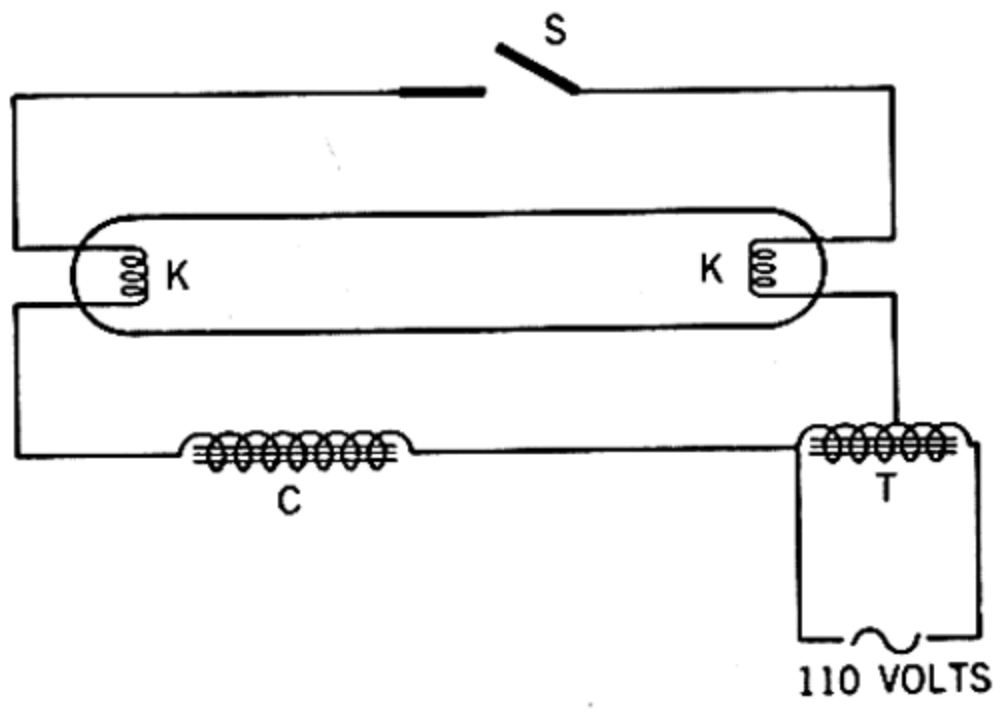

Fig. 67.—Simple circuit for fluorescent lamp.

K: Hot filament cathodes. C: Choke coil.
S: Automatic switch. T: Autotransformer.

Low voltage fluorescent lamps filled with pure neon are also manufactured. In these lamps the neon resonance lines 736 and 740 Å excite the

* The very high value of 85 per cent for the line 2537, as mentioned in one paper,[41] was probably obtained in a fluorescent tube designed for special research work and is not characteristic for commercial fluorescent lamps. It is likely that the other mercury resonance line at 1849 Å has an intensity in the discharge spectrum which should not be neglected. Very little is known about this question. Ruettenauer[42] estimates the ratio of the intensities of the lines 2537 and 1849 Å to be about 5:1, but this is not much more than a guess. According to Butaeva,[43] however, the short-wave resonance line contributes nothing to the fluorescence excitation of zinc beryllium silicate phosphors. This was apparently caused by a too great manganese concentration in the phosphor. With a lower manganese concentration the short wave-length radiation would be able to produce fluorescence, but then the yield of the fluorescence excited by the line 2537 Å would become rather small.

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[40] H. Kreft, *Z. tech. Physik*, **19**, 345 (1938).
[41] R. N. Thayer and B. T. Barnes, *J. Optical Soc. Am.*, **29**, 131 (1939).
[42] A. Ruettenauer, *Z. tech. Physik*, **19**, 148 (1938).
[43] F. A. Butaeva, *Compt. rend. acad. sci. U.R.S.S.*, **27**, 654 (1938).

fluorescence. If helium is used as carrier gas for the electric discharge in fluorescent lamps, the results are very similar to those which are obtained with neon. However, such lamps do not seem to be manufactured on a commercial scale. Pure argon on the other hand is quite unsuitable for the purpose and the same is true for the heavier rare gases krypton and xenon. For these gases the optimum of fluorescence excitation is reached at gas pressures below 0.1 mm. (Fig. 68) and at these pressures the electric

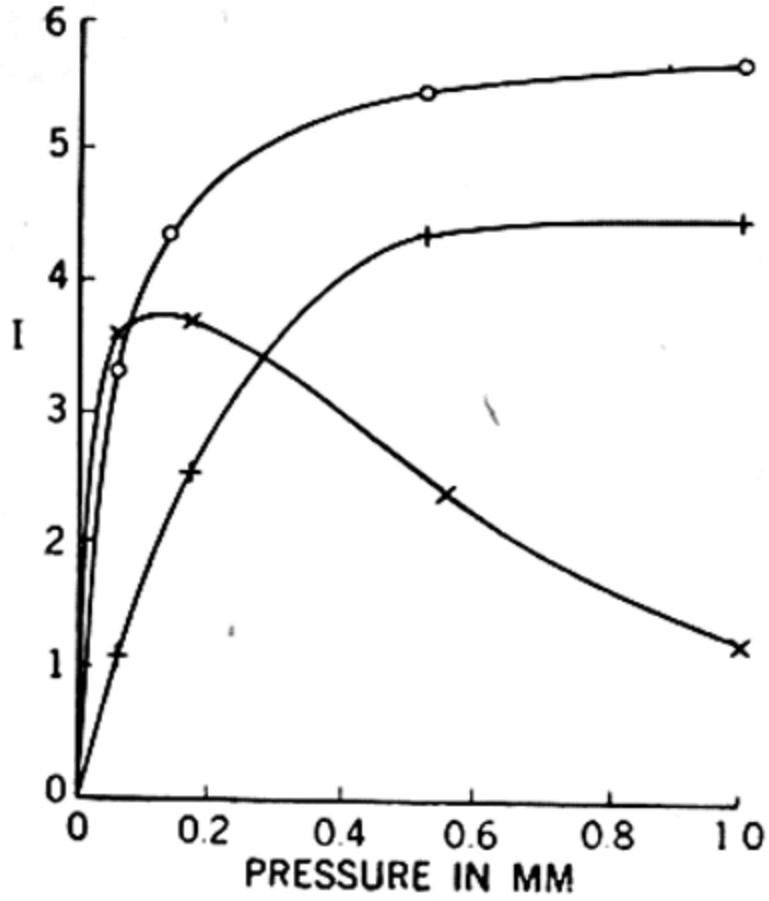

Fig. 68.—Fluorescence of Zn_2SiO_4(Mn) phosphor as function of gas pressure in rare gas discharge at 200 ma (after) Fonda and Huthsteiner).

° Helium.
+ Neon.
× Argon.

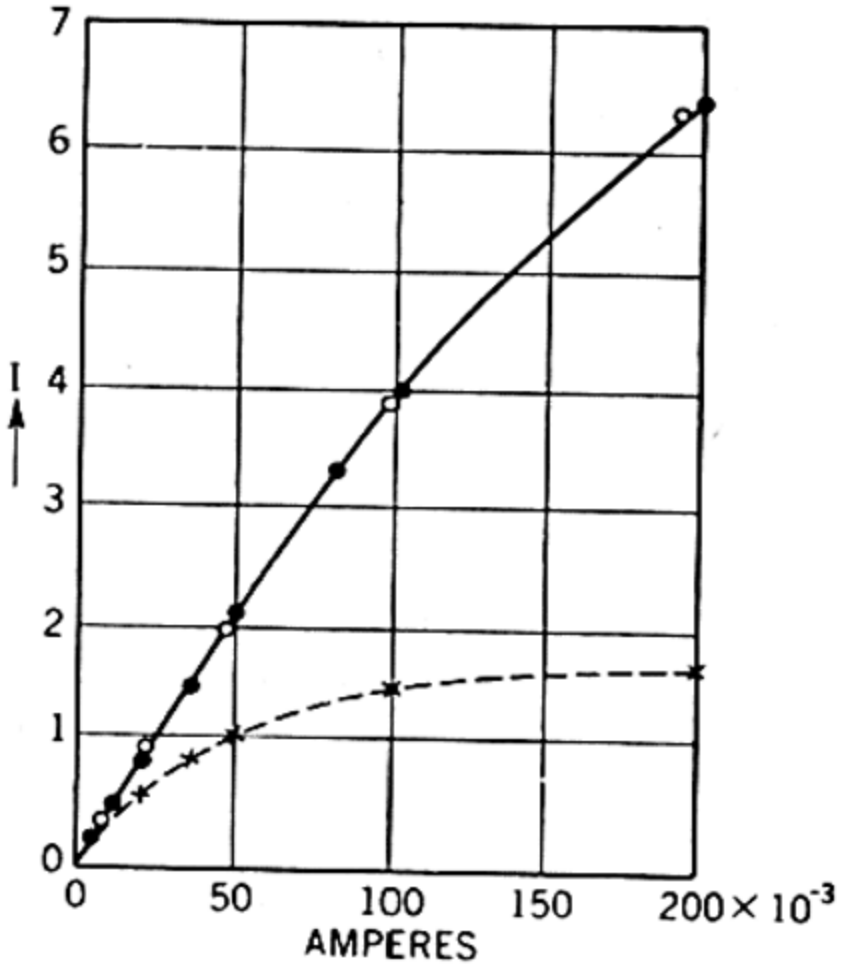

Fig. 69.—Fluorescence of Zn_2SiO_4(Mn) phosphor in low pressure gas discharge as function of current density (after Fonda and Huthsteiner).

° In helium.
• In mercury vapor.
× In argon.
Hg curve with ordinates multiplied by ½.

discharge produces a rapid "clean-up." Furthermore the highest fluorescence yield is obtained in argon at relatively small current densities and it cannot be increased beyond this value by increasing the current *[44] (Fig. 69).

* Both facts are due to the circumstance that the atoms of the heavy rare gases have a relatively great probability of being raised by electron impact into the metastable states of the triplet system which do not contribute to the emission of the resonance lines and from where the atoms can be transferred by subsequent collisions into higher states of excitation.

[44] G. R. Fonda and H. Huthsteiner, *J. Optical Soc. Am.*, **32**, 156 (1942).

High voltage fluorescent lamps with cold electrodes, operated at voltages between 600 and 3000 volts, have much smaller fields of application. Most of the data to be found in the following sections refer to low voltage mercury vapor lamps.

The aims to be attained by fluorescent lamps are twofold: the ultraviolet radiation which is always present in the spectrum of a gas discharge lamp* is made useful for the light production, and light of almost any desired hue is produced without the use of colored glasses and a corresponding loss in intensity. It must be kept in mind, however, that the energetic efficiency of photoluminescence is strictly limited by Einstein's law and becomes smaller the shorter the wave-length of the primary radiation. Under excitation by the Hg line 2537 Å, fluorescence light of optimum visibility (5550 Å) can be produced at a theoretical maximum of about

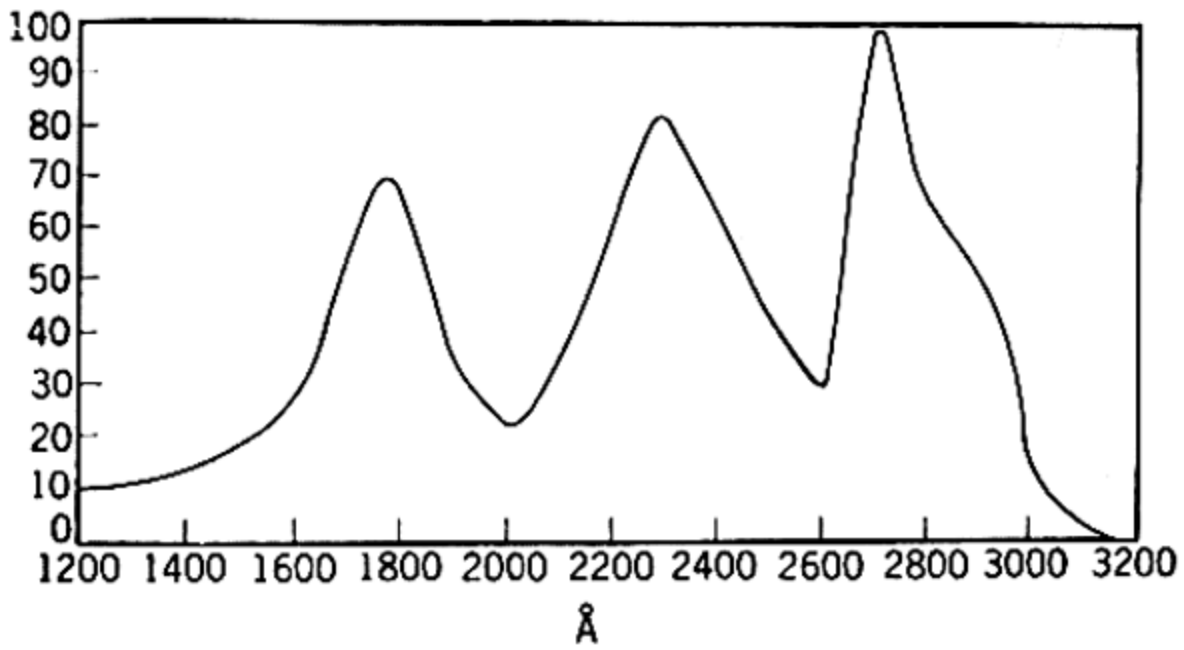

Fig. 70.—Absorption and "excitation" bands of calcium tungstate (Beese).

45%. For the neon lines 736–740 Å this value is reduced to a little over 13%. This corresponds to about 275 and 70 lumen, respectively, instead of the optimum yield of 621 lumen per watt.

On the other hand the luminescent material must be selected so that its maximum absorption coincides with the maximum ultraviolet emission of the gaseous discharge. Organic compounds are out of the question because of their instability. The ZnS and other sulphide phosphors, so serviceable for many purposes, are not very useful here because they respond best to exciting wave-lengths of the near ultraviolet and the visible spectrum. For the Hg vapor lamps the phosphors most generally used are: $CaWO_4$ (Pb), $MgWO_4$, the Mn activated silicates of Zn, Zn†

* Almost the total intensity of the radiation of gas discharge can be concentrated into the resonance line of the gas but not into any other part of its spectrum. With the one exception of the well-known yellow sodium lines, the resonance lines of all other elements are located in spectral regions unsuitable for illumination and in most cases in the ultraviolet part of the spectrum.

Be and Cd, and borates and phosphates of Cd. All these phosphors have strong absorption and excitation bands in the spectral range below 3000 Å (Fig. 70; also Fig. 44, page 87).

Different phosphors are mixed, according to the color wanted. Daylight, corresponding to a color temperature of 6500° K., is produced by a mixture of 28% white and 25% pinkish white $ZnBeSiO_4$* with 47% of blue-white $MgWO_4$. A softer and more rosy white, corresponding to a color temperature of 3500° K., is obtained by reducing the $MgWO_4$ content to 14%. Such different shades of white are used in general for apartment, office and factory illumination. For decoration and advertisement all sorts of strongly colored lights are available from violet blue to orange red. Pure red is more difficult to obtain and rather weak (Fig. 71).[45a]

For neon lamps, Mn activated zinc silicate† and calcium tungstate have so far proved most advantageous. These phosphors have a second very strong absorption or excitation band in the region below 2100 Å (see Fig. 44). The material must be of greatest purity in this case and in Zn_2SiO_4 the Mn concentration must be much lower than in the Hg lamps.[42]‡ In neon fluorescent lamps the reddish color of the gaseous discharge itself contributes an essential component to the total light output. The relative fluorescence intensity excited by the Ne resonance lines is strongest at low current density and a neon gas pressure of 1.5 mm. Under these conditions the color of the lamps is yellow with Zn_2SiO_4 and pink with $CaWO_4$, due to the superposition of the fluorescence and the neon light.[44, 45b]

In the argon-mercury vapor lamps the visible mercury lines contribute not more than 5% to the total light output.[46]

For the coating of the fluorescent powder on the glass walls of the tube two methods are used. Either the surface is precoated with a binder and the powder is blown in by a hot air blast, or the powder is mixed with a flux and coated on the surface. Organic binders like glycerin or a nitrocellulose solution are subsequently removed by heating. Inorganic binders (silicate, phosphate or arsenate compounds) are dried into a glass-like cement on which the powder remains fixed. A perfectly even and homogeneous distribution of the phosphorescent material is very difficult to obtain. The thickness of the coating should be such that the light trans-

* By changing the proportion of Zn and Be, the Mn content and the firing temperature, these phosphors can be prepared with fluorescence colors varying from yellowish white to pink.

† The zinc silicate may also be replaced by cadmium silicate or cadmium borate.

‡ See page 88.

[45a] R. L. Oetting and C. L. Amick, *Trans. Illum. Eng. Soc.*, **36**, 1369 (1941).

[45b] H. G. Jenkins and J. N. Bowtell, *Trans. Faraday Soc.*, **35**, 154 (1939).

[46] A. Ruettenauer, *Z. tech. Physik*, **19**, 359 (1938).

mission is about 50% as compared to the transmission by the uncoated glass. This would, for instance, correspond to about 5 mg. of $MgWO_4$ per square centimeter.[48]

The best solution would be to incorporate the phosphor in the glass itself. Research in this direction has been started and is still in progress,

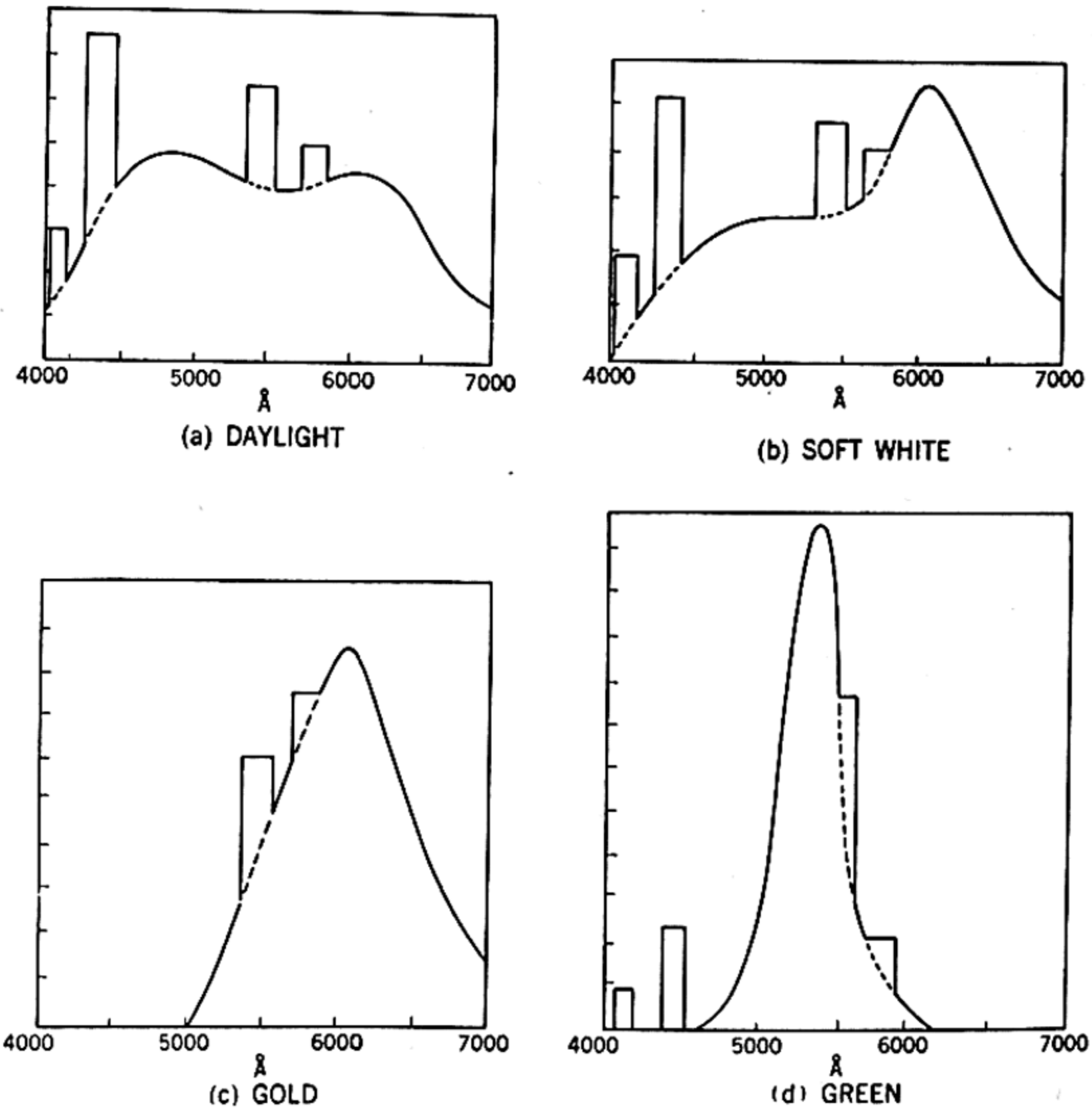

Fig. 71.—Spectral intensity distribution for different Mazda fluorescent lamps (⊓: mercury lines) (after Oetting and Amick).

but does not seem to have produced practical results so far. Canary glass, which for a long time was the only glass with a strong fluorescence, was under consideration at the beginning of the development, but for various reasons it has never been used.

The luminous efficiency of fluorescent lamps depends largely on the color of their fluorescence. Table XV gives the relative brightness of

differently colored commercial Hg fluorescent lamps. The large differences are due, mainly to the spectral distribution of the eye sensitivity, to a smaller degree to the difference in energetic yield, and partly also to a difference in quantum yield of the phosphors. Lamp dimensions and all other conditions are equal.

With the most favorable greenish fluorescence of $Zn_2SiO_4(Mn)$, argon-mercury discharge lamps attain an efficiency of 100 lumens per watt. Varying with color, tube length and other conditions, the efficiency of commercial fluorescent lamps is from 20 to 100 lumens per watt.[46, 48] A 15 watt white fluorescent lamp, 12 inches long, with a diameter of 1 inch gives a total emission of about 450 lumens (30 lumens per watt) as compared to a standard 40 watt inside frosted filament lamp with a total output of 425 lumens.[44, 49] This comparison is, however, not quite adequate, since there is an additional loss of energy of 25 to 30% in the ballast of the fluorescent lamps, so that the total input in the 15 watt lamp is about 19 watts.

TABLE XV[47]

RELATIVE BRIGHTNESS OF FLUORESCENT LAMPS

Color	Green	White	Daylight	Gold	Blue	Pink	Red
Brightness in arbitrary units	100	63	55	49	35	33	5

One part of the energy consumed in the lamp itself is spent in keeping the hot electrodes working. This "electrode potential drop" of about 15 volts is independent of the length of the discharge tube.[48] Lamps of greater length and higher watt input have therefore a somewhat higher efficiency.*

The total amount of energy consumed by a white fluorescent lamp being about $\frac{1}{2}$ to $\frac{1}{3}$ of the energy consumed by a filament lamp of the same output, the ratio between the total amounts of heat produced by each of these lamps is also $\frac{1}{2}$ to $\frac{1}{3}$. But while a filament lamp radiates 78% of its input, mostly as infrared radiation, a fluorescent lamp radiates less than 50% of the consumed energy with hardly any infrared radiation, the balance of the energy being diffused by heat conduction.[50]

Temperature has a rather considerable influence on the luminous yield

* The electrode drop for cold electrodes in high voltage lamps is of the order of 100 volts.[48]

[47] F. C. Winkler, paper presented *Second Ann. Pacif. Conf. Illum. Eng. Soc.*, 1941.
[48] J. W. Marden and G. Meister, *Trans. Illum. Eng. Soc.*, **36**, 1286 (1941).
[49] B. T. Barnes, W. E. Forsythe and W. J. Karash, *Gen. Elec. Rev.*, **42**, 540 (1939).
[50] B. Oday and R. F. Cissell, *Trans. Illum. Eng. Soc.*, **36**, 1286 (1941).

of fluorescent mercury lamps. Due to the small current density the temperature of the tube walls is relatively low. Under normal room temperature of 21 to 26° C. (70–80° F.), the glass walls are kept at 40 to 45° C. When the temperature of the environment rises, the luminous efficiency falls off slightly, mainly because of the increase of Hg vapor. pressure. The losses would become important if the free air circulation around the tube were obstructed and thus the glass temperature raised to 60 or even 100° C.*[40, 41, 51]

Because of the influence of the mercury vapor pressure, fluorescent lamps take some time (of the order from 10 to 15 min.) before they reach their equilibrium brightness. During this period the vapor pressure, which is very low (about 10^{-3}) when the lamp strikes, rises toward the value

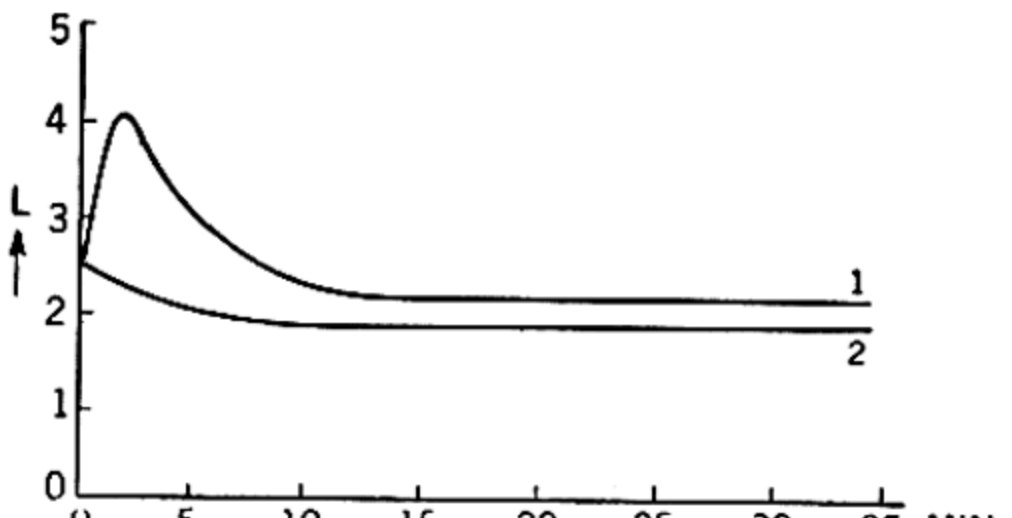

Fig. 72.—Brightness of fluorescent lamp as function of time during stabilization period of discharge (Baumgartner).
1: Bare lamp. 2: Lamp with reflector.

corresponding to the equilibrium temperature, while the emission of the resonance line and accordingly the excitation of fluorescence goes through a maximum before it reaches its stable state (Fig. 72). If two lamps are placed parallel to each other with a small interval separating them, as is frequently done for technical reasons, the time lapse within which the

* Within this temperature range the fluorescence yield of the phosphors is directly affected only very slightly. The decreasing intensity of exciting radiation due to increasing Hg vapor pressure is a rather complicated phenomenon. The mere re-absorption of the resonance radiation, which is usually made responsible, is not sufficient because the "imprisoned" radiation would be re-emitted as often as it is absorbed. The longer time of imprisonment, however, increases the probability of collisions of the excited Hg atoms either with electrons, with other Hg atoms, or with argon atoms. These collisions produce either higher excited states of the Hg atoms with subsequent emission of visible light, or the formation of Hg_2 molecules with subsequent emission of Hg_2 bands or the transfer of the excitation energy into heat.

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[51] J. W. Marden, N. C. Beese, and G. Meister, *Trans. Illum. Eng. Soc.*, **34**, 55 (1939).

equilibrium is reached becomes somewhat shorter and the final brightness of the lamps is a little lower, because of the mutual heating effect. The curve of Fig. 72 refers to a bare lamp; by enclosing it in a reflector the stable condition is attained still faster, so that the maximum in the curve of Fig. 72 disappears completely, and the equilibrium brightness is 4 to 10% lower than for the bare lamp.[52] p.[52]

In fluorescent neon discharge lamps the luminous yield is necessarily a good deal lower than in the mercury vapor lamps. Apart from the unfavorable short wave-length of the Ne resonance lines, even the quantum yield does not exceed 25% in this case, according to Ruettenauer, while Fonda and Huthsteiner estimate it as being of the same order as in Hg vapor fluorescent lamps, or not much below 100%.

To a certain degree this deficiency may be compensated by the fact that the neon lamps are much less influenced by temperature and that they are not subject to the steady depreciation of luminous output which is characteristic for the mercury vapor lamps. The effect has been ascribed to the deposition of finely divided mercury on the fluorescent surface, but is probably due, at least in part, to the formation of a surface film by some chemical reaction of excited Hg atoms and a component of the phosphor, probably oxygen. The phosphorescent powders themselves are practically indestructable under normal lamp operation. The decrease of light output is strongest during the first 100 hours, when it may amount to about 10%, but continues during the whole life of the tube.[48] If the current is kept constant, however, the brightness of commercial fluorescent lamps is sufficiently constant after a "seasoning" period of 100 hours that their use could be recommended for single point temperature checks of optical pyrometers. The apparent brightness temperature of the central part of a 15 watt pink fluorescent lamp (Gen. Elect. Co.) is 1110° C. (2030° F.), with deviations of not more than ±5° for individual lamps. It does not vary appreciably during 180 hours of continuous operation or 540 cycles of intermittent operation (10 min. on, 10 min. off).[53]

TABLE XVI

LUMINOUS YIELD OF A FLUORESCENT LAMP AS A FUNCTION OF TIME.
1 x 18 INCHES, 4 MM. ARGON + H_G, M_GWO_4

Time in hours	3	75	267	888	1365	1704	3000
Lumen per watt	41.8	37.7	38.0	36.7	35.3	34.9	29.0

[52] G. R. Baumgartner, *Trans. Illum. Eng. Soc.*, **36**, 1341 (1941).
[53] C. F. Lucks and H. W. Russell, *J. Optical Soc. Am.*, **30**, 163 (1940).

The lamp life is influenced by several factors, among which the life of the activated electrodes is one of the most important. In the average it is rated at the present time as 2500 hours.[54]

The light emission of ordinary gas discharge lamps, like neon tubes, mercury tubes, etc., follows the fluctuations of the applied alternating voltage completely even up to very high frequencies. At the usual frequency of 60 cycles very disagreeable stroboscopic effects are thereby produced. The same problem occurred in the case of fluorescent lamps, but it was possible to eliminate it to a certain degree by the use of luminescent material with an afterglow lasting longer than the half period of the alternating current. As compared to incandescent filament lamps, the light output of fluorescent lamps is much less affected by small variations of line voltage. 1% change in line voltage produces a change of about 1.5% in light output.*

Notwithstanding their high efficiency, the brightness of fluorescent lamps is relatively small. On the average it is below 5 candle powers per square inch. This means that for the same light output the tubes are much longer than incandescent bulbs. In general 1 to 2 inches wide, they have lengths from 12 inches to 48 inches and more.

High voltage fluorescent lamps, with a diameter of $\frac{1}{2}$ or $\frac{1}{4}$ inch, must have at least a length of 10 meters if their efficiency is to be comparable to that of the low voltage lamps. They are occasionally used for the illumination of large machine shops or offices, but because of their high intrinsic brightness they can hardly be recommended for such purposes. High voltage fluorescent lamps are employed to better advantage in restaurants, show windows or for outdoor signs, where decorative effect and not efficiency is the primary condition.[55]

As a matter of fact the introduction of all kinds of fluorescent lamps, so different in shape and light distribution from the usual filament lamps, has presented a great many new problems to the illuminating engineer. Such problems, however, are beyond the scope of this book.†

* In a gas discharge a decrease in voltage corresponds in the first approximation to a proportional decrease in energy or in the number of excited atoms or finally in light output. In an incandescent filament it corresponds to a decrease in temperature, and the luminous output of a glowing lamp filament is proportional to the 16th power of its absolute temperature.

† See for instance the reports and discussions of the 35th convention of the Illuminating Engineering Society at Atlanta (*Trans. Illum. Eng. Soc.*, **36**, 1286–1461, 1941).

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[54] *E.g.*, E. W. Briggs, *Trans. Illum. Eng. Soc.*, **36**, 1354 (1941).

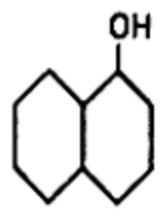
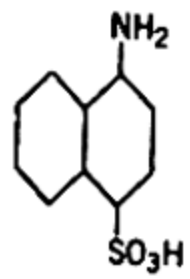
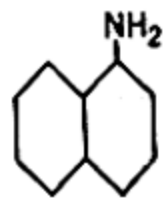
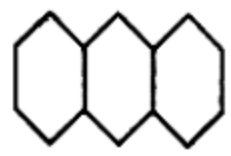
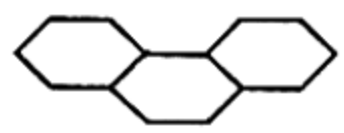
[55] D. P. Caverly, *ibid.*, **36**, 1298 (1941).

LIST OF IMPORTANT FLUORESCENT MATERIALS

A. AROMATIC HYDROCARBONS AND HETEROCYCLIC COMPOUNDS

Table XVII

Aromatic Hydrocarbons and Heterocyclic Compounds (Neutral in Liquid Solution)

Name	Formula	Fluorescence Bands, Å	Excitation,* Å	Fluorescence Color	Page
1. Benzene		6 bands from 2600–3000	2600	U.V.	28, 100
2. Naphthalene		12 bands from 3000–3650	33000	U.V.	73, 100
3. α-Naphthol		3900–5600 with peak 4100	4000	blue	117
4. α-Naphthionic acid		4000–5600 with peak 4500 in alkaline solution	4000	blue green	117
5. α-Napthylamine		3900–5600 with peak 4100	4000	blue	73, 117
6. Anthracene (pure)		4 bands 3800–4550	3800	violet	28, 73, 100 et seq.
(commercial)		(naphthacene bands)	(4360)	(green)	109, 131
7. Phenanthene (pure) (commercial)		3 bands 3460–4068 (anthracene bands)	3500	deep violet (blue)	102, 108

*Long wave-length limit of excitation.

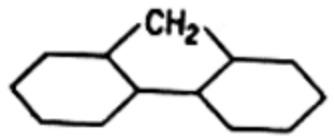
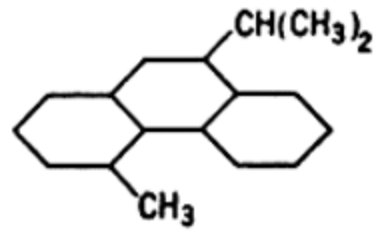
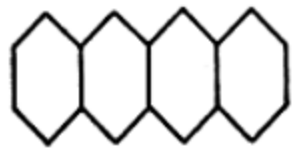
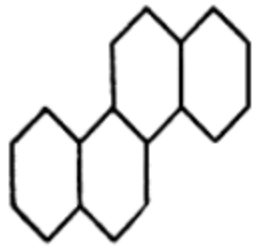
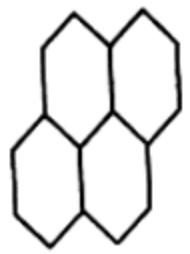
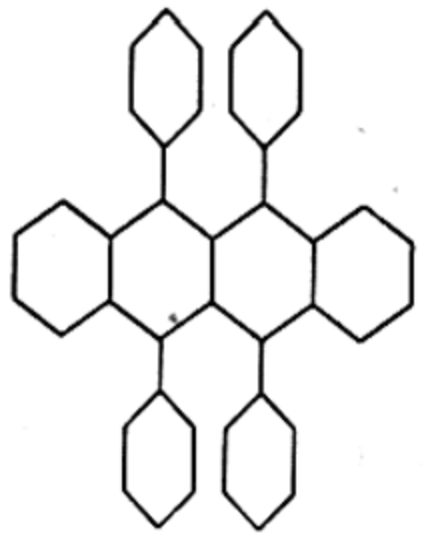
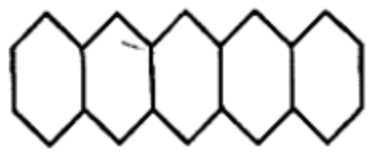
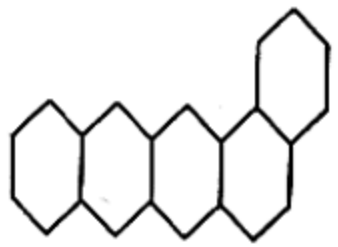
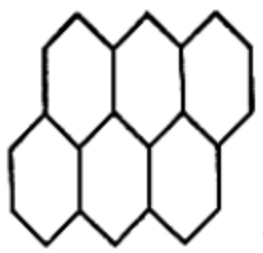
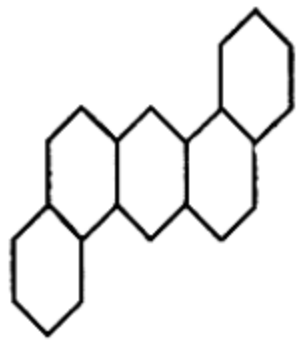
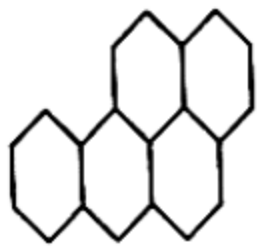
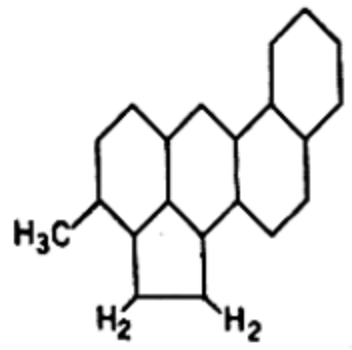
8. Fluorene (pure) (commercial)		3020–3700 (anthracene bands)	2940	U.V. (blue)	28, 108 158
9. Retene		3 bands 3400–3700		U.V.	102
10. Naphthacene		4 bands 4500–6500	4360	green	28,73,100 et seq. 109,131
11. Chrysene (pure) (commercial)		3 bands 3600–4000 (anthracene bands?)		deep violet (blue)	108, 131
12. Pyrene		5 narrow bands 3700–4000		U.V.	102
13. Rubrene		5300–6500 with peak 5900	5600	yellow	28, 73

TABLE XVII—*Continued*

Name	Formula	Fluorescence Bands, Å	Excitation, Å	Fluorescence Color	Page
14. Pentacene		?		red	
15. Dibenzanthracene				yellow green	101
16. Anthanthrene				blue	73
17. Dibenzanthracene		3 bands 3900–4600		blue	101
18. Benzopyrene		4 band groups 4000–4320		blue violet	101
19. Methyl cholanthrene		broad band 4000–5200 with peak at 4600		greenish blue	102

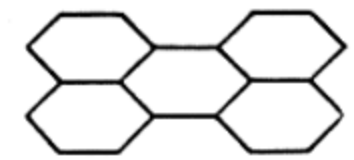
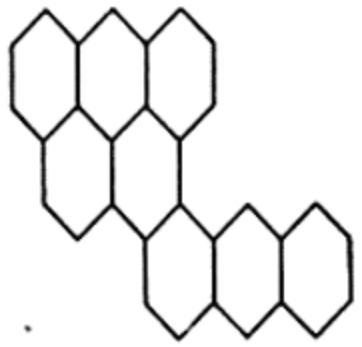
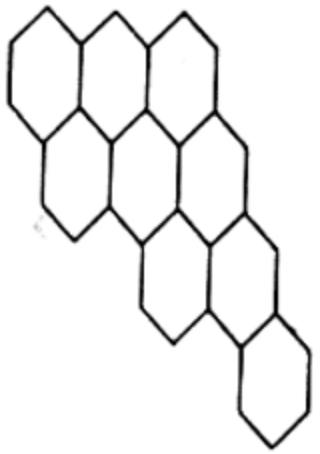
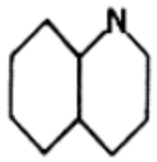
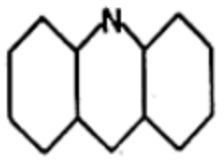
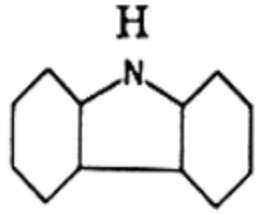
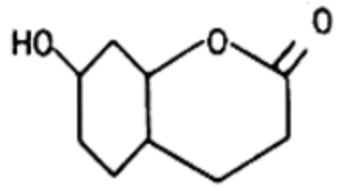
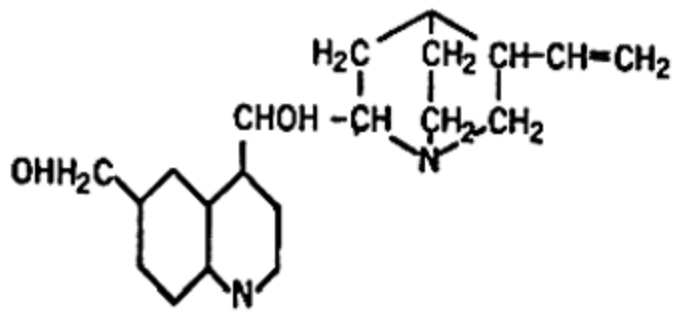
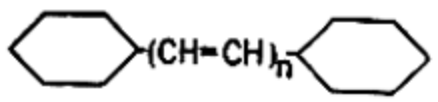
20. Perylene		4400–4700		violet	72
21. Pyranthrene				green	72
22. Violanthrene				green	72
23. Quinoline		3850–4900		blue	72
24. Acridine in acid solution		broad band 4000–4800 with 4 peaks broad band 4500–5500 with 4 peaks		blue green blue	72, 107 107
25. Carbazole		broad band 4000–4700 with two peaks		dark blue	72, 101
26. Umbelliferone				blue	105, 117

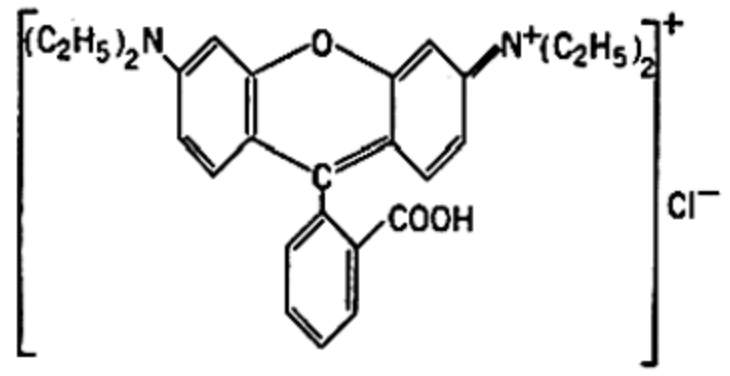
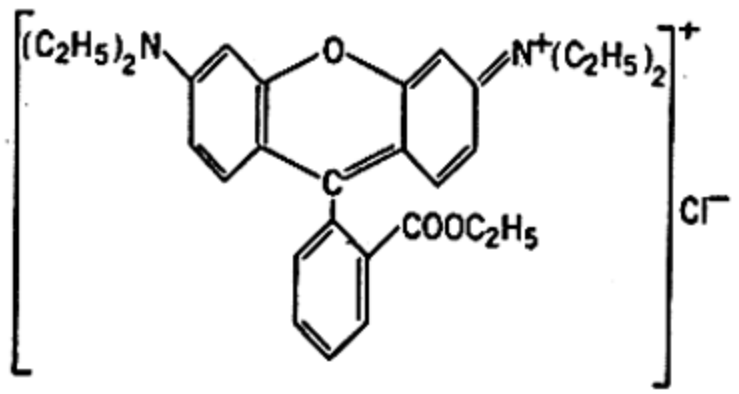
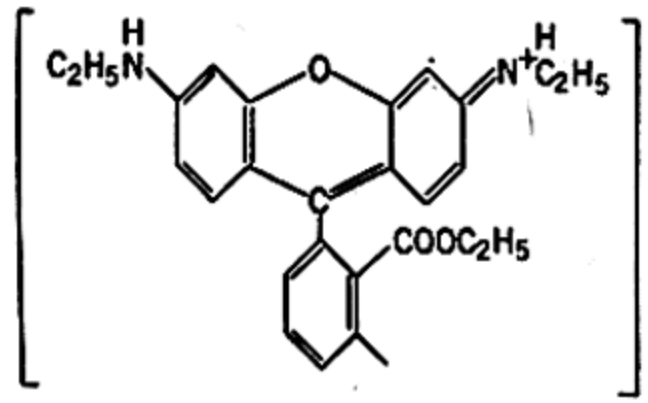
TABLE XVII—*Concluded*

Name	Formula	Fluorescence Bands, Å	Excitation, Å	Fluorescence Color	Page
27. Quinine (in water)		4000–5000		violet	106, 115 et seq.
(in acid solution)		4200–6700 with two peaks 4660 and 5500		whitish blue	117 et seq., 132
28. Diphenyl-polyenes		Bands with 4 peaks			
n = 1		3300–4300		violet	72
n = 2		3600–4800		blue violet	
n = 3		4500–6500		sky blue	
n = 4		5000–7000		yellow green	
n = 5		6000		yellow	

B. SYNTHETIC AND NATURAL DYESTUFFS

Table XVIII

Synthetic Dyestuffs in Solution

	Colour index No.	Name (Molecular Weight)	Formula	Fluorescence		Page
				Wave-Length of Band (of Peak), Å	Color	
1.	746	Rhodamine B extra (446.5)		5500–7000 (6050)	red	28, 57 73, 122 127 et seq., 132
2.	751	Rhodamine 3 B (501.5)			orange	73, 135
3.	752	Rhodamine 6 G (450.5)		(5800)	yellow	73, 127 et seq., 132

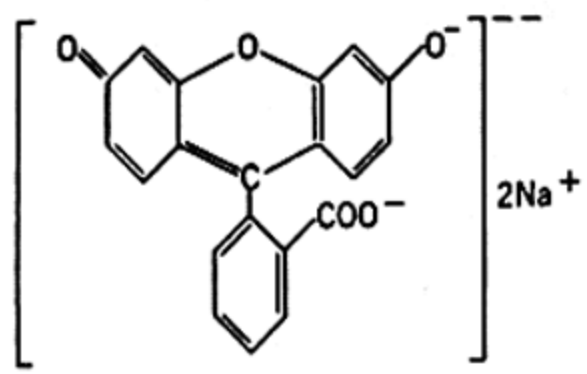
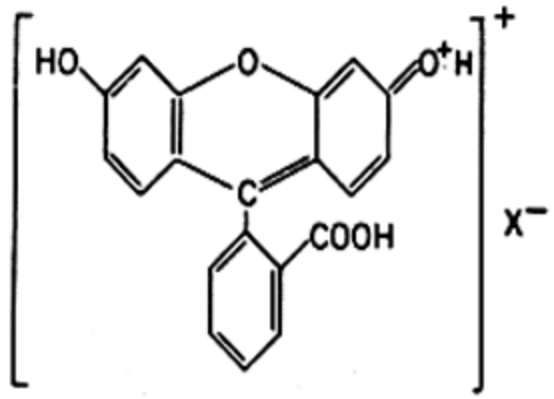
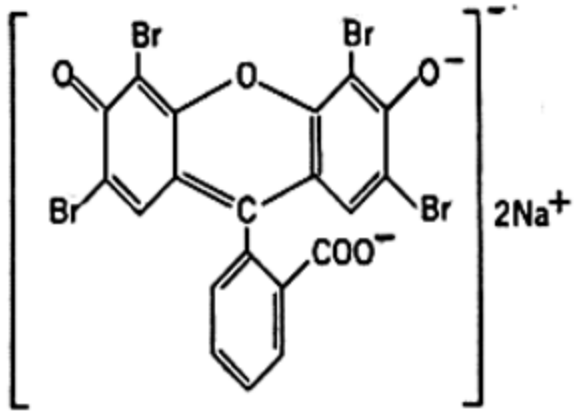
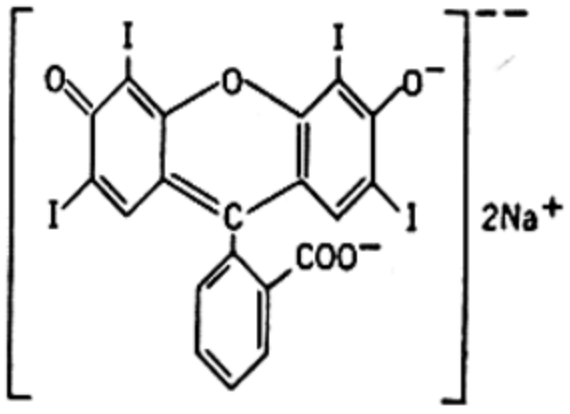
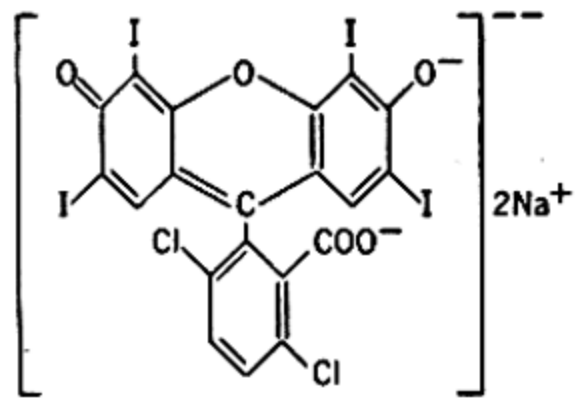
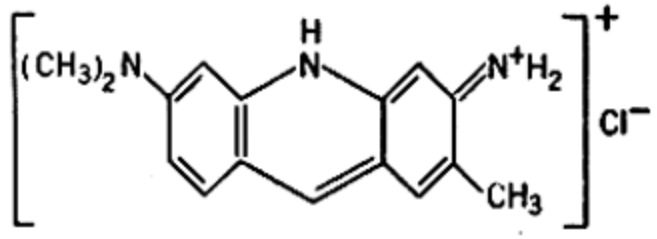
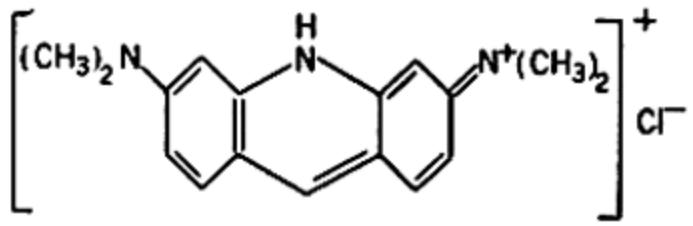
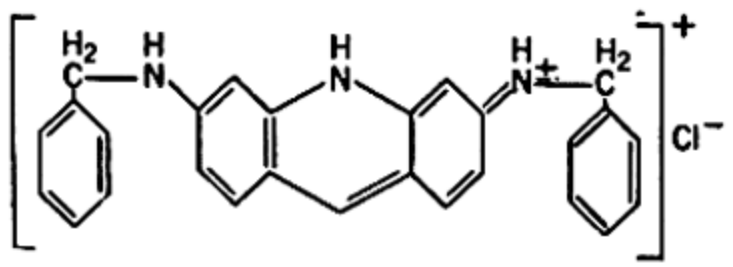
4.	766	Fluorescein in alkaline solution (370)		5000–6000 (5270)	yellow green	18, 28 67, 73 114, 127 et seq.
5.		Fluorescein in acid solution (370)		4500–5600 (4800)	blue green	114, 116
6.	768	Eosin G extra (692)		5400–6400 (5800)	yellow (5800)	28, 67 73, 116 128
7.	773	Erythrosin (879.4)		5000–6000 (5600)	yellow	28, 72 et seq. 129

TABLE XVIII—*Continued*

	Colour index No.	Name (Molecular Weight)	Formula	Fluorescence: Wave-Length of Band (of Peak), Å	Fluorescence: Color	Page
8.	779	Rose bengale (902.5)		5400–6700 (5900)	yellow	73, 129
9.	787	Choriphosphine O (287.5)			green	67, 73
10.	788	Euchrysine 3 R (Acridine orange) (301.5)		(5850)	yellow green	73
11.	789	Aurophosphine (453.5)			green	67

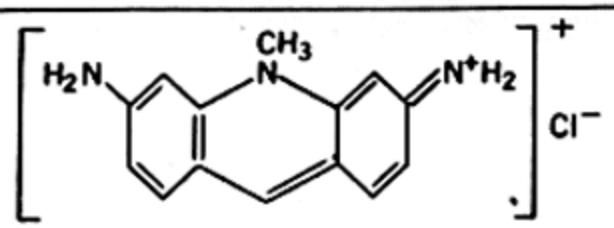
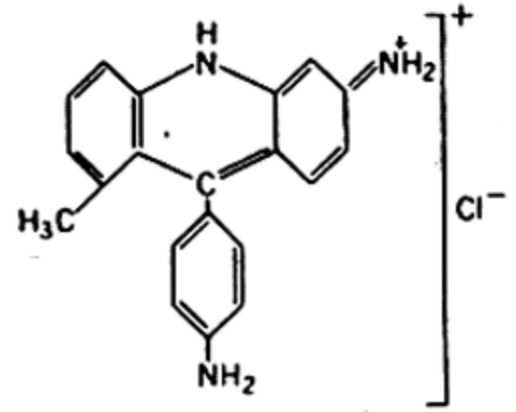
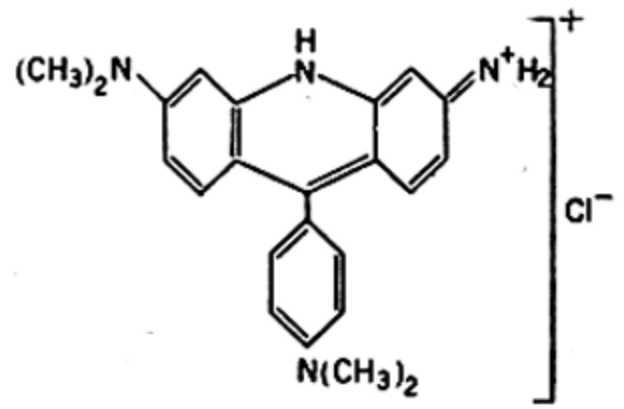
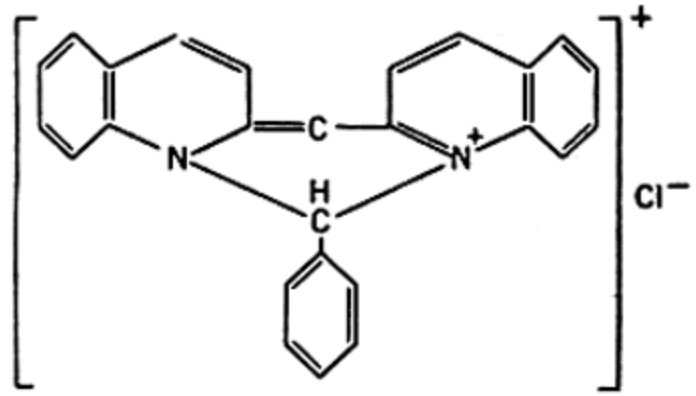
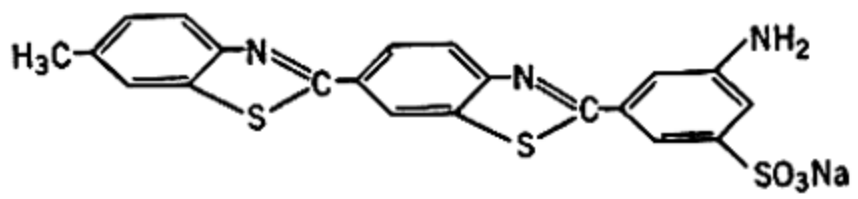
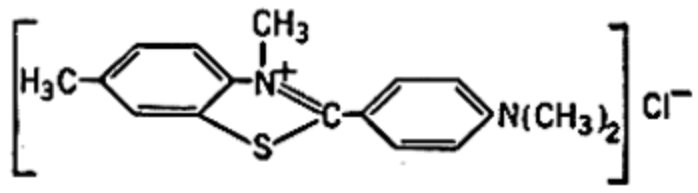
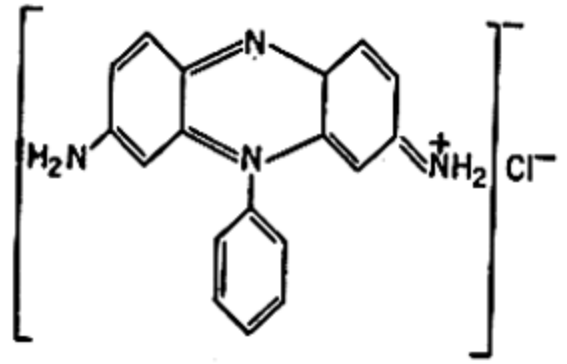
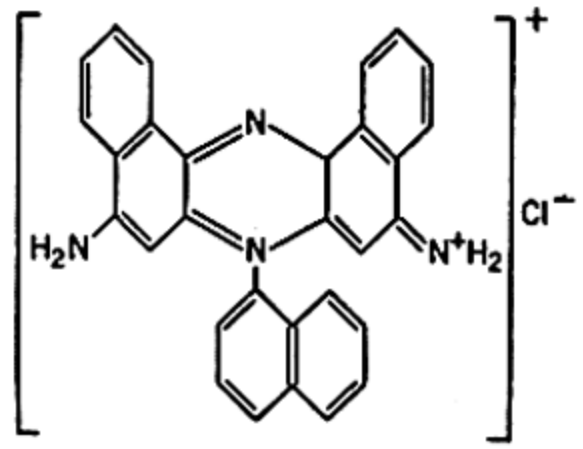
12.	790	Trypaflavine (259.5)		4600–5800 (5200)	yellow green	67, 73 110, 127
13.	794	Flavophosphine (335.5)			green	
14.	795	Rheonine A (fast phosphine) (392.5)			green	
15.	805	Azalin (quinoline red) (394.5)			orange red	

TABLE XVIII—*Continued*

	Colour index No.	Name (Molecular Weight)	Formula	Fluorescence: Wave-Length of Band (of Peak), Å	Fluorescence: Color	Page
16.	812	Primulin yellow in acetone in water (475)			blue green (violet)	67, 73 127, 131
17.	815	Acronal yellow S (thioflavin S)			green	67, 127
18.	816	Rhoduline yellow (Thioflavin T) (318.5)			green	67, 73
19.	827	Safranine B extra (322.5)			yellow green	73
20.	848	Naphthyl blue (on silk)			red	
21.	857	Magdala red (475.5)		5500–6600 (5940)	orange red	73

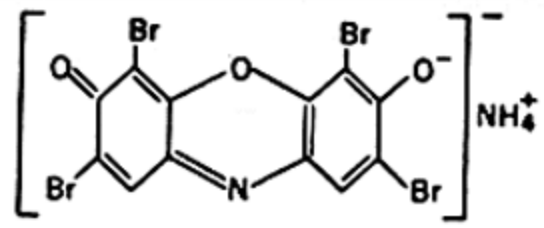
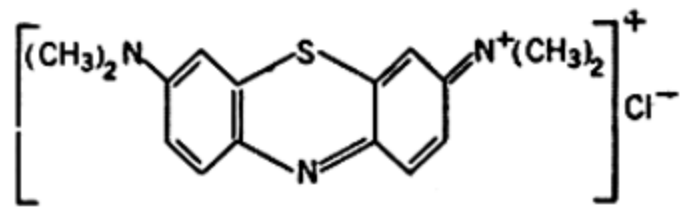
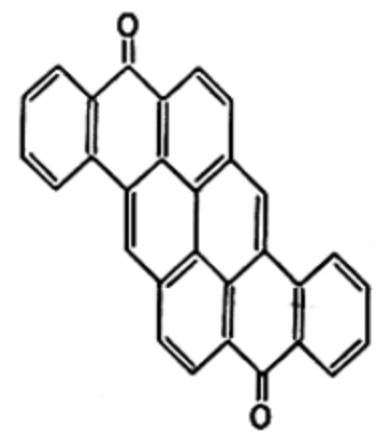
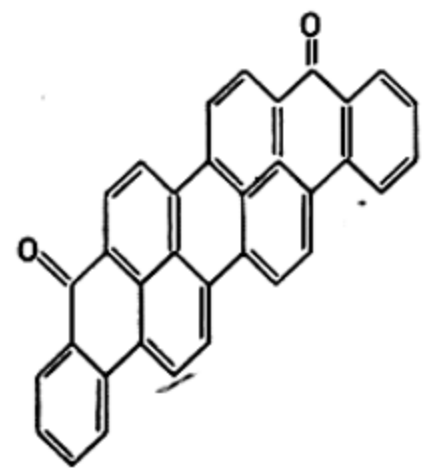
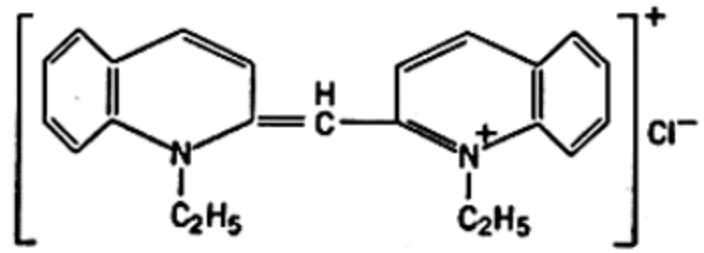
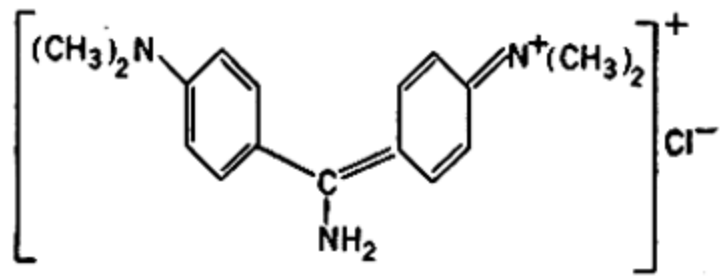
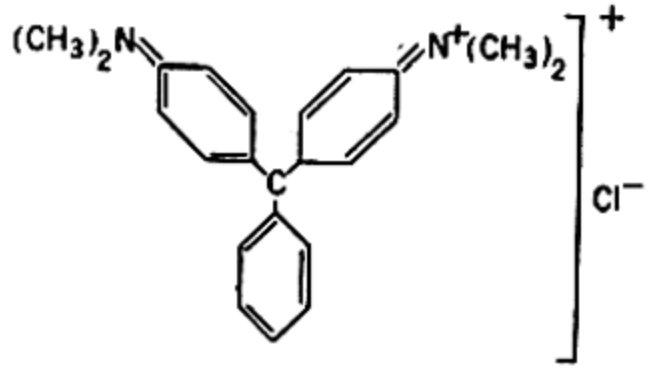
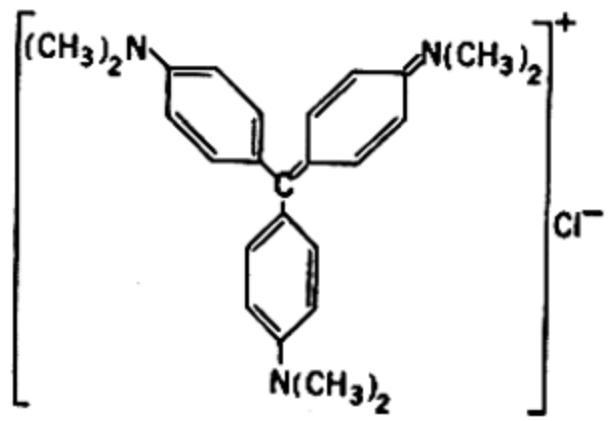
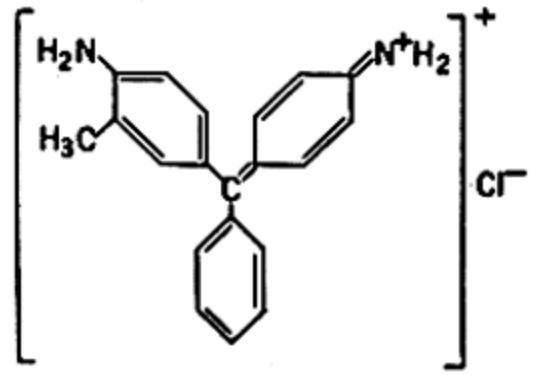
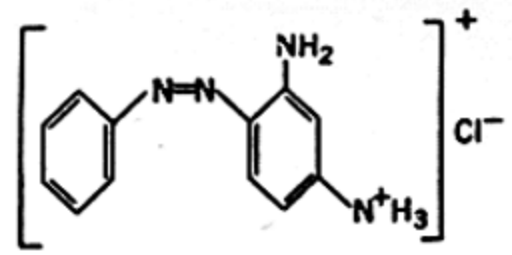
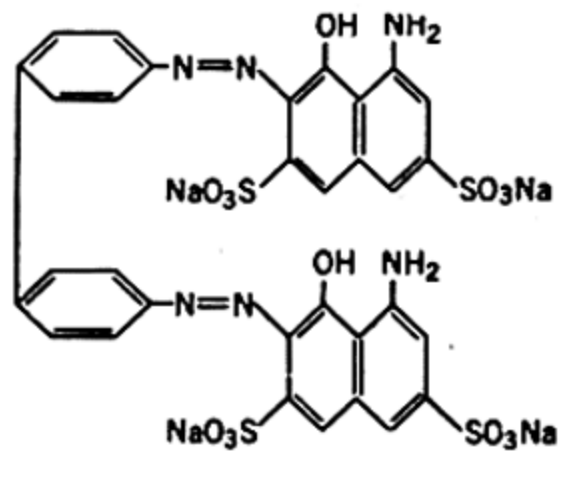
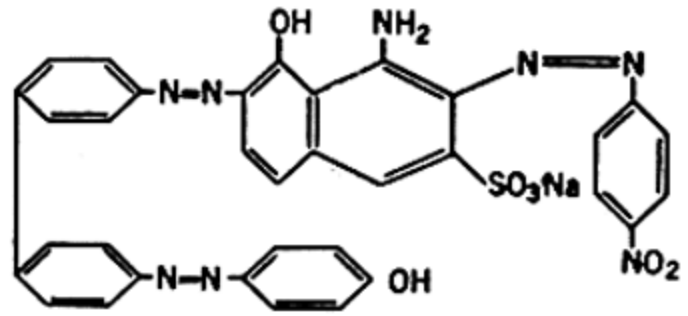
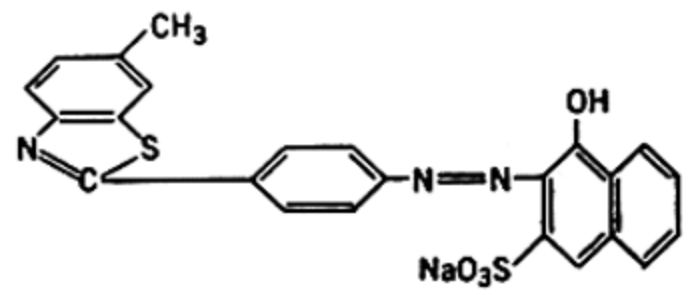
22.	908	Fluorescent blue (546)			red	
23.	922	Methylene blue (329.5)		(6700)	red	28, 73
24.	1066	Pyranthrene (indanthrene gold orange) (406)			green	73
25.	1099	Violanthrene B.S. (456)			red	73
26.	1288	Soledon jade green (on cloth)			green	
27.	867	Pseudo-iso-cyanine* (362)		narrow band 5720	yellow	

TABLE XVIII—*Concluded*

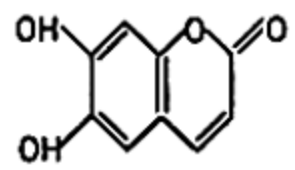
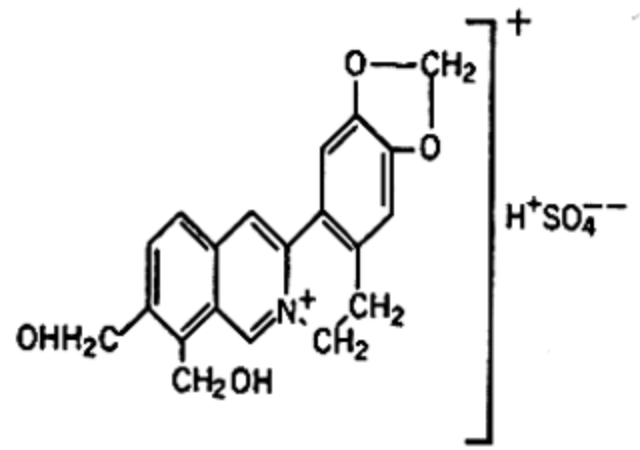
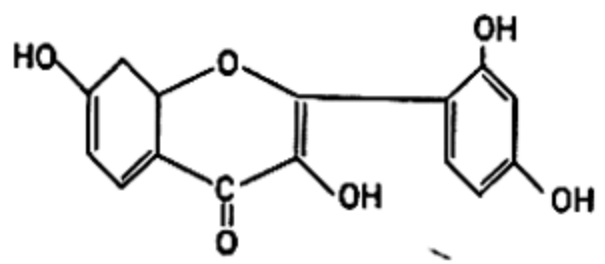
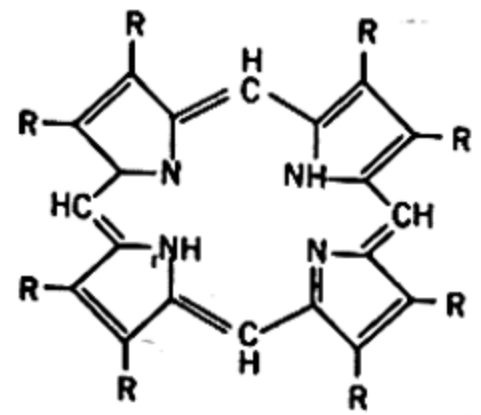
	Colour index No.	Name (Molecular Weight)	Formula	Fluorescence		Page
				Wave-Length of Band (of Peak), Å	Color	
28.	655	Auramine** (303.5)		4900–5900	green	73, 124 131
29.	657	Malachite green** (364.5)		4750–5800	green	73
30.	681	Crystal violet** (407.5)		6000–7600 (6700)	red	73
31.	734	Fuchsine** (322.5)		5550–6650	orange	

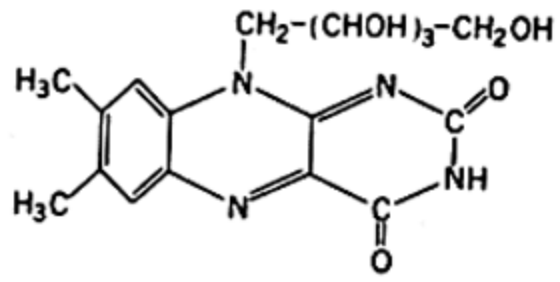
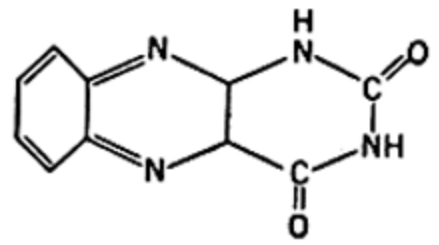
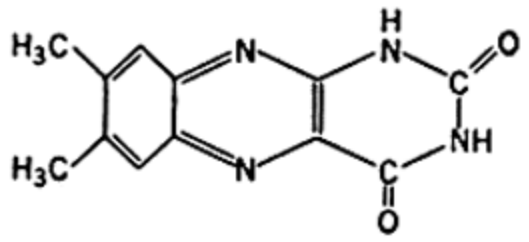
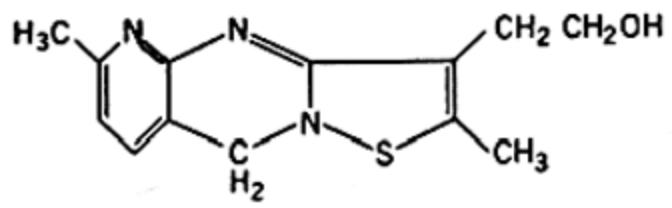
32.	27	Chrysoidine*** (248.5)			green	
33.	406	Direct sky blue***				
34.	520	Direct blue 2B*** (908)				74
35.	594	Dianil green† (710)			color varies with nature of cloth	74
36.	127	Geramine G† (465)				74
37.	716	Benzoblue 4GL†				74

* Polymerized at high concentrations in water.
** In solid solutions or adsorbed on solid adsorbents.
*** When adsorbed on solid adsorbent.
† When dyed on wool, silk, cotton or rayon.

Table XIX

Natural Dyestuffs in Solution

	Formula	Fluorescence		Page
		Wave-Length of Band, Å	Color	
1. Aesculin		4000–5500 (4900)	blue	34, 57, 70, 117, 129
2. Berberine bisulfate			yellow green	67
3. (1231) Fisetin*			yellow	74
4. Porphyrins				
neutral or alkaline solution		series of narrow bands 5900–6900	orange red	28, 74
acidified solution		3 bands 5800–6600	orange yellow	103, 115

5. (1299) Chlorophyll		3 bands 6300–8300	red	74, 102, 127
6. Urobilin (zinc complex)		3 bands 5150–6400**	green	105
7. Riboflavin (vitamin B_2)		symmetrical band 5000–6000 (5620)	greenish yellow	27, 74, 112 et seq., 115, 120
8. Alloxazine			blue	103, 115
9. Lumichrome 6,7-Dimethyl-alloxazine		4540–5470	sky blue	103, 115 120
10. Thiochrome (derived from thiamin or vitamin B_1)			sky blue	74, 104 112

* Only when adsorbed on solid adsorbent.

** The band at 5200 Å is by far the strongest.

C. INORGANIC COMPOUNDS AND MINERALS

TABLE XX

SYNTHETIC INORGANIC PHOSPHORS

	Basic Material	Activator	Color of Luminescence	Peak of Luminescence Band, Å	Excitation Spectrum, Å	Page
1.	CaS	Mn	orange	6000	near U.V. to 4200	81 et seq., 90, 136 et seq., 141
2.		Cu	green	5100	near U.V. to 4200	81 et seq., 90, 136 et seq., 141
3.		Ni (less than 10^{-5})	deep red	7800	near U.V. to 4200	
4.		Bi	blue	4750	near U.V. to 4200	81 et seq.
5.	SrS	Mn	green yellow	5550	near U.V. to 4200	81 et seq.
6.		Cu	blue green	5350	near U.V. to 4400	81 et seq.
7.		Ag	violet	4200	near U.V.	81 et seq.
8.		Bi	blue green	5200	near U.V. to 4400	81 et seq.
9.	ZnS	pure	light blue	4650	near U.V.	15, 32, 79 et seq., 133
10.		Ag	blue	4450	near U.V.	20, 28, 31, 80 et seq., 151, 157
11.		Cu	green	5200	near U.V. to 4300	28, 80 et seq., 141 et seq., 145, 148, 150
12.		Mn	orange	5850	near U.V. to 4500	80 et seq.
13.	(Zn + Cd)S	Ag	all colors from blue to red with increasing Cd concentration			20, 84
14.		Cu	all colors from green to red see Table X, p. 84			84

15. (Zn + Cd)S	Mn	orange	5900	near U.V. to 4600	60, 85
16. Zn_2SiO_4	Mn	green	5250	below 2960	28, 34, 85, 146, 155, 158, 163, 165, 167
17.	Mn	yellow	5630	below 2960	80 et seq., 85 et seq.
18. $CdSiO_3$	Mn	pinkish yellow	5950	below 3200	28, 85 et seq., 165
19. (ZnBe)SiO_4*	Mn	yellow white	5950	below 3000	28, 31, 86 et seq.
20. $CaWO_4$	(Pb)	blue	4400	below 3000	28, 31 et seq., 79 et seq. 90, 132, 145
21. $CdWO_4$	—	whitish blue		below 3000	145
22. $MgWO_4$	—	whitish blue	4800	below 3200	80 et seq., 158, 164 et seq.
23. $CaMO_4$	—	yellow			81, 90
24. CdB_2O_4	Mn	pink	6150	below 3600	28, 89, 165
25. ZnB_2O_4	Mn	red or green		below 3600	81, 91, 165
26. $MgSiO_3$	Mn	red		2800	81
27. $Cd_3Zn_3(PO_4)_2$	Mn	red		below 3000	81, 91, 165

* By partially replacing Zn in Mn-activated zinc silicate phosphors by Be, Cd, Zr, or Ti or by several of these elements and by partially replacing Si by Ge, and further by varying the heat treatment, the color of luminescence can be varied between all shades of green, yellow and white.

Table XXI

Pure Inorganic Compounds. Excitation Spectrum: Near U.V. to Blue

	Fluorescence Color	Visible Fluorescence Spectrum, Å	Strongest, Å	Page
1. Eu*	orange red	6 line groups 5890–7560 (and infrared)	5900–6200	77, 96
2. Sm*	orange yellow	6 line groups 5580–7830 (and infrared)	5900–6000	77, 96
3. Tb*	green	6 line groups 4800–6800	5400–5500	77, 96
4. Dy*	greenish yellow	4 line groups 4790–7775 (and infrared)		77, 96
5. Gd*	all U.V.	(5 narrow lines between 3115 and 3150)		77, 96
6. Pr**	orange	irregularly spaced lines 4820–7225 (and infrared)	5950–6420	77, 96
7. Nd**	little visible (infrared) and U.V.)			96
8. Tu**	violet	band-like line groups 4000–8000 (and U.V.)	4580 (3500–3750)	92
9. Er**	blue	diffuse lines 4000–5600		96
10. Uranyl compounds*	greenish yellow	5 to 7 equidistant band groups, first and last weak	4700–6900 ($\Delta\nu$-840cm.$^{-1}$)	15, 57, 78, 97 et seq., 155
11. $BaPt(CN)_4 + 4H_2O$***	green	broad diffuse band	4850–5670	24, 78, 145
12. $MgPt(CN)_4 + 5H_2O$	orange	broad diffuse band	5000–6000	78

* As pure solid salts, in liquid and solid solutions. (Trivalent compounds)

** Only in solid solutions. The last two little characteristic. (Trivalent compounds)

*** As solid crystals only. Liquid solutions, see page 78. Many other Pt cyanides are fluorescent, but they have been little used.

Table XXII

Natural Gems and Minerals

Substance	Color of Fluorescence	Fluorescence Spectrum, Å	Excitation	Page
1. Ruby (Al_2O_3, Cr)	red	2 strong lines 6927, 6942 surrounded by weaker lines and bands	near U.V. to green	4, 81, 98, 123
2. Spinel ($MgAl_2O_4$, Cr)	red	1 strong line 6855 surrounded by weaker lines and bands		98
3. Alexandrite ($BeAl_2O_4$, Cr)	red	2 strong lines 6785, 6803 surrounded by weaker lines and bands		98
4. Disthene (Al_2SiO_5, Cr)	red	2 strong lines 6886, 7060 with a few broad bands on both sides		—
5. Emerald [$Be_3Al_2(SiO_3)_6$, Cr]	red	2 strong lines 6806, 6835 surrounded by few weak lines and broad bands		98
6. Uwarowite [Ca_3(Al, Cr) $(SiO_4)_3$]	red	2 strong lines 6971, 7016 broad continuous background		—
7. Sapphire (Al_2O_3, Ti)	orange red	band 6000–6800 with peak at 6400		98
8. Autunite (uranyl calcium phosphate)	greenish yellow	typical uranyl bands as above	U.V. to blue	97
9. Schroeckingerite (hydrous uranyl carbon-	greenish yellow	typical uranyl bands as above	U.V. to blue	97
10. Torbernite (uranyl copper phosphate)				
11. Uranophane (uranyl calcium silicate)	greenish yellow	typical uranyl bands as above	U.V. to blue	97
and many others, containing the uranyl	greenish yellow	typical uranyl bands as above	U.V. to blue	97
12. Scheelite	whitish blue	like synthetic $CaWO_4$	below 3000	100, 120
13. Willemite*	green	like zinc silicate phosphors	below 3000	100, 120
14. Fluorite*		lines of Gd, Eu, Tb and other rare earths or blue or green bands	near U.V.	4, 91, 132
15. Calcite*		red, green, yellow bands		4, 91, 99
16. Hiddenite } lithium aluminum silicate	purple			91, 99
17. Kunzite } lithium aluminum silicate	reddish yellow	broad band, peak 5900		91, 99

* The fluorescence, though sometimes very brilliant, is only accidental in these minerals and due to some impurity. Other samples of the same mineral are not fluorescent.

Title [redacted]

Author [redacted]

Accession No. [redacted]

Call No. [redacted]

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AUTHOR INDEX

SUBJECT INDEX

(The more important fluorescent and phosphorescent substances are listed in tables XVII to XXII with references to pages and are not mentioned in this index. "fl" stands for fluorescent or fluorescence, "ph" for phosphorescent or phosphorescence.)